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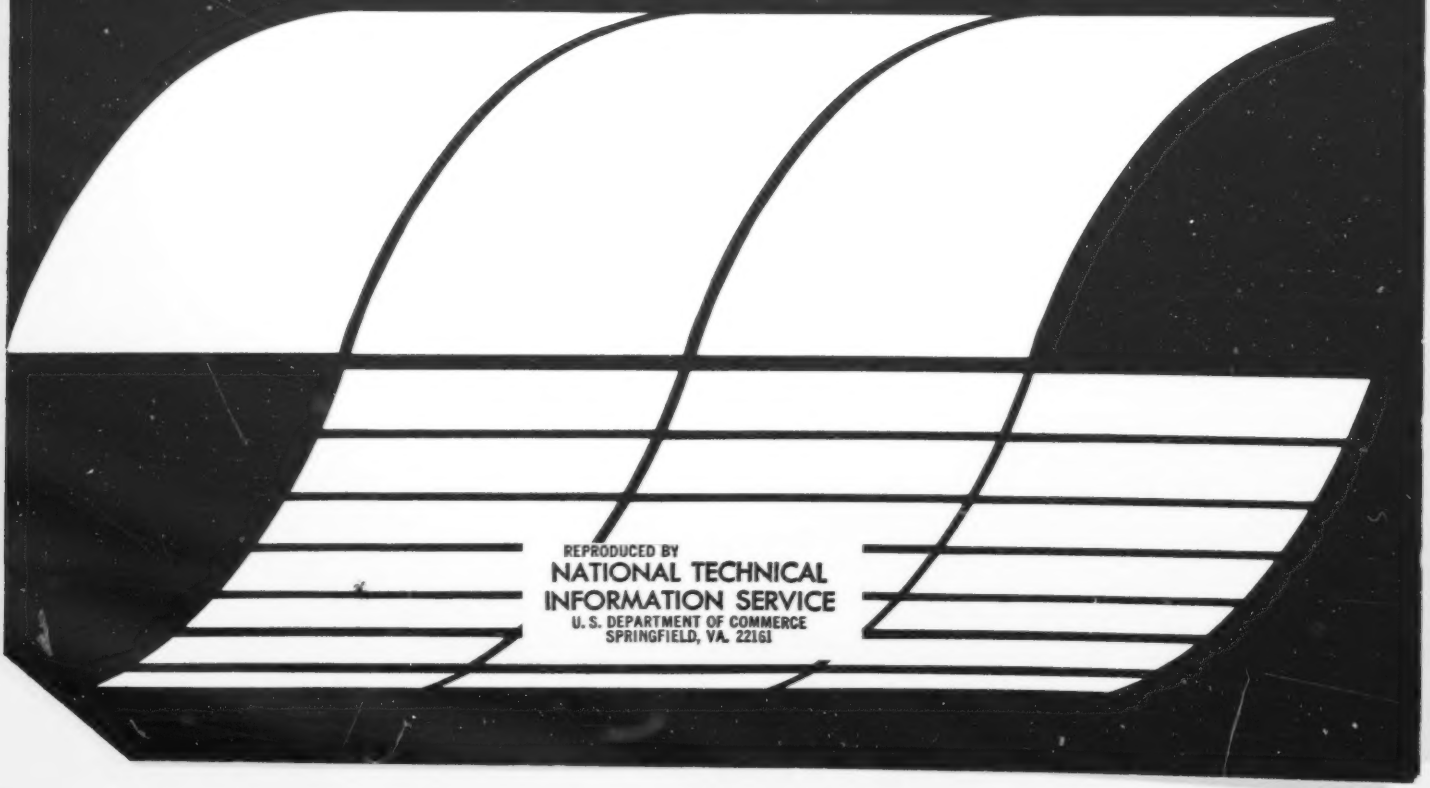

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The purpose of the program was to determine what standards are currently available, their suitability for validating present in-situ water quality measurements, and to assess the accuracy of measurement traceability from the in-situ instrument to a recognized standard.

The ease with which in-situ systems gather large volumes of data pertinent to environmental studies, pollution monitoring, and other applications is such that their continued use and growth is assured. Because their use is recent, inattention to establishing standards has made suspect the absolute accuracy of the data and thus, the comparability between data sets. Most users have devised their own techiques of assuring the relative accuracy of their in-situ data, but no recognized standard techniques exist.

It was found that deficiencies exist in two areas: (1) lack of an adequate (multiple point) primary standard for some parameters (e.g., salinity, dissolved oxygen); and (2) failure by in-situ system users to follow standard methods (where they exist) for calibration and standardization.

The study recommends the establishment of standard reference materials and methods for calibration and standardization to assure accuracy of parameters measured in-situ. It is further recommended in the study that development of specific means to achieve the traceability to standards be initiated.

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EVALUATION OF PRESENT CHEMICAL STANDARDS IN RELATIONSHIP TO IN SITU MARINE WATER QUALITY MEASUREMENTS

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DISCLAIMER

This report was assembled by the Test and Evaluation Laboratory, National Ocean Survey, National Oceanic and Atmospheric Administration, from information received under contract with the Ocean Engineering Division, Interstate Electronics Corporation, Anaheim, California. Approval does not signify that the contents necessarily reflect the views and policy of the National Oceanic and Atmospheric Administration or the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The Department of Commerce, National Oceanic and Atmospheric Administration (NOAA), has been given the responsibility to monitor seawater pollution related to energy exploration and development. In situ measurements of chemical parameters are becoming more important because of the large volumes of data which are required for monitoring seawater pollution, but which cannot be achieved with conventional discrete sampling and subsequent laboratory analysis. The more detailed information that is needed to understand the complex chemical processes involved requires that sensors be used for continuous in situ monitoring and/or profiling with depth. Inevitably, however, some confusion exists about the accuracy and precision of data collected from different in situ instrument arrays. Present standards, calibration procedures, and uncertainties in the data collected with in situ water quality systems, as well as how these standards, calibration procedures, and systems contribute to this confusion, will be evaluated in this report. Parameters most commonly measured and those which show promise for future development are discussed.

James P. Sullivan
Contracting Officer's Technical
Representative
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Oceanic and Atmospheric Administration

ABSTRACT

This report represents the findings determined by Interstate Electronics Corporation Oceanic Engineering Division during a 9-month study entitled "Evaluation of Present Chemical Standards in Relationship to In Situ Marine Quality Measurements" (Contract 6-35234), performed for the U.S. Department of Commerce, National Oceanic and Atmospheric Administration (NOAA). The purpose of the program was to determine what standards are currently available and their suitability for validating present in situ water quality measurements, and to assess the accuracy of measurement traceability from the in situ instrument to a recognized standard. The assessment included the determination of measurement uncertainty and resulted in recommendations for the development of necessary standards.

While development and use of in situ measurement systems in the marine environment is in its infancy, the ease with which in situ systems gather large volumes of data for environmental studies, pollution monitoring, and other applications is such that their continued use and growth is assured. Because their use is recent, inattention to establishing standards has made suspect the absolute accuracy of the data and, thus, the comparability between data sets. Most users have devised their own techniques of assuring the relative accuracy of their in situ data, but no recognized standard techniques exist.

It was found that deficiencies exist in two areas: (1) lack of an adequate (multiple point) primary standard for some parameters (e.g., salinity and dissolved oxygen); and (2) failure by in situ system users to follow standard methods (where they exist) for calibration and standardization. The study recommends: (1) the establishment of standard reference materials and methods for calibration and standardization to assure accuracy of parameters measured in situ; and (2) the development of specific means to achieve traceability to these standards.

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LIST OF ABBREVIATIONS

ABBREVIATIONS

ASTM	-- American Society for Testing Materials
CalCOFI	-- California Cooperative Fisheries Investigation
CI	-- confidence interval
cm	-- centimeter
CTD	-- in situ conductivity, temperature, and depth measuring system
CUE	-- Coastal Upwelling Experiment
DMRP	-- Dredged Material Research Program
DO	-- dissolved oxygen
GEOSECS	-- Geochemical Ocean Sections
Hz	-- Hertz
I.A.P.S.O.	-- International Association of the Physical Sciences in the Ocean
KHz	-- kiloHertz
kg	-- kilogram
mA	-- milliampere
mg/l	-- milligram per liter
MIL/STD	-- military standard
ml	-- milliliter
mm	-- millimeter
mS/cm	-- millisiemens per centimeter
mv	-- millivolt
NA	-- not available
NBS	-- United States National Brueau of Standards
NORPAX	-- North Pacific Experiment
OCS	-- Outer Continental Shelf
ppm	-- parts per million
ppt	-- parts per thousand
QC	-- quality control
SI	-- The International System of Units
SRM	-- standard reference material
STD	-- in situ salinity, temperature, and depth measuring system
TDWG	-- Test Documentation Working Group

LIST OF SYMBOLS

SYMBOLS

°C -- temperature in degrees Celsius

Eh -- oxidation reduction potential in millivolts

KCl -- potassium chloride

n -- number

Na_2S -- sodium sulfide

O_2 -- oxygen

% -- percent

‰ -- parts per thousand

pH -- negative logarithm of hydrogen ion concentration

Vac -- alternating current voltage

Vdc -- direct current voltage

ACKNOWLEDGMENTS

Because of the amount of interest and the number of personal contributions to this study, it is impossible to acknowledge individually all of the contributors to the program. In addition to the information generously provided by instrument manufacturers throughout the world, there were over 300 personal communications from correspondents in the United States and 24 foreign countries. This evidence of worldwide interest in accurate oceanic measurements should provide the necessary incentive to develop uniformly accepted calibration and standardization techniques.

The staff of the Oceanic Engineering Division would like to express special thanks to the volunteers from Saddleback College and Fullerton College, the teams of marine technicians for the experimental cruise, Moss Landing Marine Research Center, LFE Environmental, Inc., and the following instrument manufacturers who provided instruments:

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SECTION 1

INTRODUCTION

Under this study, Interstate has considered the chemical parameters (dissolved oxygen and pH) and two supporting physical parameters (temperature and salinity) which are routinely measured in situ in the marine environment. The study evaluated present standards in relationship to these water quality measurements, and has explored the traceability of those standards. While this study emphasizes investigation of dissolved oxygen, pH, temperature, and salinity, it is noted that currently 19 parameters are measured in situ, and 59 other parameters are under consideration. Estimates of the range and accuracy required of in situ measurement, present and future, were determined by surveying major groups using in situ sensors and by reviewing manufacturer's recommended procedures and published specifications.

In situ marine monitoring systems remotely sense the oceanic parameters, or transferable property from which the parameter can be derived, while the sensor package is submerged. Frequently considered as in situ monitoring are those pumped systems that provide a continuous flow from the location of interest. Sub-classes of in situ monitoring systems can be characterized by the nature of the platforms (unmanned moored buoys, drifting buoys, or manned ships) or by the method of measurement (automated, continuously profiling systems, or towed systems). User contacts reveal a significant increase in the use of continuous profiling systems for coastal zone water quality measurement and for pollution control and monitoring. While they are a relatively recent innovation, they deserve special consideration because of their potential.

Today's emphasis on conservation of the marine environment results in the greatest number of measurements being made in the relatively shallow waters of the coastal zone, where depths typically are less than 50 meters. The vertical gradients of water properties in shallow bodies of water are frequently great and can vary widely over short time spans. Therefore, there is considerable interest in maintaining accuracy and in sampling at short intervals. Since rapid sampling frequency cannot be met using conventional discrete sampling techniques such as Nansen casts, there has been an increase in the use of continuous profiling systems. A brief description of two classes of in situ instrumentation is provided in Appendix A.

The design of profiling systems integrates the sampling process with onboard data processing and analysis. This is highly desirable in order to cost effectively meet the mission objectives of some users, such as wastewater treatment districts that perform nearly continuous monitoring at outfalls. The cost of post-survey data analysis by hand methods is prohibitive

and introduces unacceptable errors. The automatic data reduction and analysis capabilities of the continuous profiling systems results in great quantities of data quickly and neatly produced and ready for user interpretation. Of significant importance in saving labor costs is the system's ability to print the data on the various Federal, State, and local government report forms with a minimum of hand labor, such as typing and drafting of charts.

A discussion of the components of error in and between in situ systems and a demonstration during an experimental survey of the errors induced by different participants using different in situ instruments under nonstandard procedures are offered as a compelling argument for the procedural recommendations that follow. Because of difference in usage of a number of terms such as "Precision Standard" and "Calibration," definition of selected terms as they are used in this report appear in the glossary. The pertinent cruise data which form the basis for comments in the text are included in Appendix B.

SECTION 2

CONCLUSIONS

1. An addendum to the contract document states, "What the Government needs to know is that if a measurement is made in situ, would one get the same answer if a sample were taken at the same place and the same time and analyzed in a laboratory with laboratory methodologies?" The results of this study answers this question with an emphatic "NO!" While this situation must be remedied, a successful solution will require a well-planned, long-term commitment from the Federal Government that includes recognizing the importance of data quality in the evaluation of proposals, grants, and Government conducted oceanographic measurement programs.

2. In situ measurement is not at a state of routine data comparability between different instruments measuring the same parameter or for a single instrument operating at different time intervals. Accuracies attained are less than desirable for absolute measurements associated with research activities. The relative accuracy of in situ systems, coupled with their ability for continuous sampling and rapid data collection, is often justification for their use in monitoring programs or for coastal research programs.

3. Inter-user calibrations are not presently part of routine survey operations. The GEOSECS program does come close to the practice by centralizing the responsibility for the calibration and maintenance of instrumentation used by all investigators within the program. However, there is no interface with investigators outside the program who may utilize the data.

4. Standard reference materials and/or calibration methods are not utilized by institutions or programs. Variations in standardization methods may exist. This situation is very widespread. Manufacturer's specifications and recommendations vary; users' application of manufacturers' recommendations varies as well. Data derived from in situ measurements of a parameter by different instruments or by different programs do not seem to be comparable.

5. For current monitoring needs, adequate standards are currently available for temperature and pH. There are inadequate, multiple-point standard reference materials for salinity and dissolved oxygen.

SECTION 3

RECOMMENDATIONS

A comprehensive program plan for quality assurance must be developed for in situ marine water quality measurements, their calibration, and standardization. This program should be under the guidance of a single agency oriented to the marine environment to insure the goals will be attained. Observations of past programs of similar nature conducted by committees of agencies reveal that the dilution of authority results in failure to achieve the objectives. Program elements would include:

CALIBRATION AND STANDARDIZATION MATERIALS

The program must include a standard reference material with well-defined accuracy for all parameters. Specifically:

1. Develop a series of standards for salinity that encompass the range from 0 to 40 ppt in 5-ppt increments with an accuracy to 0.002 ppt.

2. Develop a series of dissolved oxygen standards for the range from 0 to 10 ppm in increments of 2 ppm with an accuracy of 0.05 ppm.

CALIBRATION PROCEDURES

Instrument calibration procedures utilized on Government-funded programs must be required to satisfy traceability to accepted standards and have formal documentation. A major source of error in any system is the calibration and standardization routine. The military and space programs have used this type of procedure for many years. These programs require manufacturers to develop a recommended calibration procedure which is verified, with the calibration traced to a recognized standard. The verification process is commonly conducted by an independent calibration laboratory or at the manufacturer's facility under the supervision of a Government inspector. The verification process also recommends calibration frequency. Inputs from the manufacturer for calibrating marine in situ monitoring instruments would be considered by the agency responsible for procedure development. Current user practices for calibration would also be considered for the procedural development.

It is expected that responses from users and manufacturers will be diverse and dependent on instrument capabilities and on program accuracy requirements. But these must be considered for the development of a uniform procedure. For example, the frequency of calibration may vary with class of required measurement and type of instrumentation. A temperature sensor may

require recalibration and certification once a year to ensure 0.5°C accuracy, or as frequently as bimonthly for an accuracy of 0.02°C.

The verification of instrument calibration could be indicated by a certified seal or sticker. The sticker provides information on the date of calibration and the required date for recalibration. The official calibration procedures should be distributed by a central issuing agency that is responsible for receiving and updating as required.

Questions that require resolution of differences between methods would be resolved by a Test Documentation Working Group (TDWG) that includes representatives from the sponsoring agency, instrument designers, standards organization, instrument test operators, and data users. In addition to the development of calibration procedures, the TDWG would provide information on future requirements for parametric standards and sponsor the development of standards.

DOCUMENTATION PROCEDURE

A standard documentation procedure with the information basic to assessing data quality includes:

1. The standard reference material used including the date of receipt and handling since receipt.

2. A uniformly practiced and accepted Calibration and Intercalibration Procedure which would include method accuracy and precision, the frequency required for calibration, and the time lapsed since the previous calibration. The calibration procedure must also include specific instructions for field standardization procedures. The field standardization procedure should include the limits of acceptable variation.

3. A standard data reporting format including the number of replicates, mean and standard deviation of the calibration, and standardization procedure.

SUPPORT SERVICES

The sponsoring agency should consider undertaking the following program support:

1. Preparation of guidelines for evaluation of proposals for marine water quality measurement to insure that a proportion of any project is dedicated to calibration of instruments and to the supporting tasks for data quality assurance. It is strongly recommended that data quality assurance requirements be listed in the contract specifications.

2. Compilation and maintenance of a comprehensive directory of manufacturers and users of in situ chemical oceanographic instrumentation and the data types and quality resulting from these programs.

3. Preparation of test, calibration, and standard traceability procedures for in situ instruments.

4. Preparation and maintenance of a comprehensive handbook on marine instrumentation and procedures.

5. The organization and scheduling of seminars to transfer this technology to the user community.

SECTION 4

TRACEABILITY OF CALIBRATION TO COMMON STANDARDS

STANDARD REFERENCES

In situ measurements in the marine environment are subject to most of the problems that degrade laboratory measurements, with additional problems attributable to field conditions. Investigation of the error sources and their effect on the accuracy of the measurement can be classified as qualitative or quantitative, following the Shewhart (1) concept. The number assigned to a distance or a chemical concentration is quantitative. Qualitative sources of error arise from the apparatus, reagents, operator, sequence of operations, and ambient conditions involved in quantifying the measurement.

A statement on the accuracy of the quantitative number is an indication of the information content of that number within the framework of the intended application. The application will usually dictate the degree of accuracy sought and the effort required to achieve it [Eisenhart (2)]. The accuracy achievable when calibrating a system of measurement to a primary reference material with an assigned value (systematic error) depends on the precision of the measurement technique and operation involved, as well as on the accuracy of the assigned value of the primary reference material.

In making a measurement, the individual involved must take care to assure the measurement is of a unique property and not a combination of properties, such as interference from other sources (specificity). Second, no systematic errors should be permitted to cause a bias in the distribution of repeated measurements of the property. Third, the degree of precision, which is the ability to reproduce the same number on repeated measurements of the same material, must be at least as good as the desired accuracy of measurement. When these three aspects of the measurement process are assured, the accuracy of the measurement can approach its state-of-the-art level.

Accuracy is measured by referencing a measurement to a standard using a methodology that has been shown to achieve acceptable results. The practice of establishing reference standards (the primary reference units and the methodology of measurement) has been set out in some detail at the National Bureau of Standards (NBS) by Cali et al (3). The development of a measurement system has five major components as stated by NBS:

°Component 1: A Rational, Self-Consistent System of Units of Measurement. International agreement suggests this system should be the System Internationale de Unites (SI) [Cali et al (3)].

°Component 2: The Materials Necessary to Realize in Practice the SI Units and Their Derivatives. In much of the world, these well-characterized materials are called Standard Reference Materials (SRM's) and

are prepared, measured, and certified, in most instances, by national standards laboratories. The key characteristic of an SRM is that the properties of interest be measured and certified on the basis of accuracy. At NBS there are three routes that are used to accomplish this goal:

(a) Measurement of the property using a previously validated reference method. By definition, a reference method is a method demonstrated to be accurate and reproducible.

(b) Where previously established reference methods do not exist, two or more independent, reliable measurement methods are used. A reliable method is one of high precision, but one whose systematic biases have not been fully discovered and evaluated.

(c) The third route is a variation of the second. Where a previous issue of an SRM is available to be used to assure intralaboratory quality control, many laboratories can be formed in an ad hoc network to perform the work. Each laboratory uses the method felt to be most reliable (and accurate) under that laboratory's operating conditions, but must run the known SRM in parallel with the unknown as a check. The results will be used only when the certified value of the prior SRM is obtained.

°Component 3: Reference Methods of Measurement Used With or Based on SRM's. A reference method is defined as "a method of proven and demonstrated accuracy." These have been called umpire methods, referee methods, standard methods, and so forth. Absolute accuracy, implying methods with no systematic biases, is an unattainable goal, not achievable by mortals. It is important to realize that the cost of obtaining greater accuracy increases exponentially. Therefore, only that degree of accuracy required should be sought, making allowance for advances in the state-of-the-art. A good guideline is to strive for a reference method whose accuracy is three times better than that currently required by the end user. The definition and development of reference methods is a time-consuming, expensive, and complex process, involving the following steps:

(a) A group of experts surveys the literature to choose a candidate method--one expected to have small systematic biases. They also decide what the accuracy goal should be for the reference method, considering the required end use.

(b) A central laboratory is chosen to coordinate the work; develop the statistical design; prepare and distribute samples that have been previously measured by the central laboratory using an independent method of known accuracy, but one not usually available to the field in question; and distribute the SRM (a necessary precondition being the availability of the appropriate SRM).

(c) The group of experts, in conjunction with the central laboratory, writes the first version of a detailed procedure (protocol) and helps select a group of measurement laboratories (usually 6 to 10

laboratories) willing to cooperate in performing the work called for in the protocol.

(d) The central laboratory distributes the protocol, sample, SRM, and instructions to the cooperating laboratories. The cooperating laboratories perform the work according to a schedule. The analytical data plus other pertinent information are returned to the central laboratory.

(e) The group of experts and qualified personnel from the central laboratory, including statisticians, analyze the data, identify sources of error, then revise the protocol to eliminate the errors.

(f) Steps d and e are repeated as often as necessary until the accuracy goal is achieved.

(g) The protocol is written in final form and published in a journal, a collection of reference methods, or another appropriate publication.

°Component 4: Establishment of Compatibility into a Wider Area of Technology via the SRM and Reference Method. Components 1, 2, and 3 are sufficient in themselves to bring about accurate measurements in a few well-qualified laboratories. The real problem is, however, to improve the quality of and make compatible the measurement in the average laboratory on a routine basis. There are two aspects to this problem, one involving the field (routine) methods per se, the other concerned with commercially produced (in-house) working standards.

As reference methods and SRM's become available, responsible groups should begin the assessment of the various field methods currently in use. When the test materials to be used in the assessment process are characterized on an absolute (accuracy) basis via the reference method and SRM, the inaccuracies of the tested field methods will become readily apparent.

°Component 5: Assuring the Long-Term Integrity of the Measurement Process. Measurement systems are notorious in one respect--unless carefully monitored, they tend to get out of control. Loss of precision is usually the first indication that the measurement process is not in a state of quality control. In most measurement laboratories, this question is one of almost daily concern and one that has been extensively studied and addressed. Although each individual laboratory must ultimately be responsible for assuring its own quality control, professional societies and governmental agencies can, and often do, provide a mechanism that helps to assure, to a degree, long-term control.

If SRM's and reference methods are available, the mechanism for assuring the long-term integrity of the measurement process in a large number of measurement laboratories is quite straightforward:

(a) The sponsoring or testing agency prepares a series of test samples incorporated in a suitable matrix that cover the range of values likely to be encountered in real life.

(b) The properties are determined by the sponsor's laboratory (or laboratories) using the reference method to obtain values of known accuracy.

(c) The test samples, as unknowns, are distributed with suitable instructions and reporting forms to the laboratories under test who perform the work as instructed. In true blind studies, these samples will not be differentiable from daily, routine samples.

(d) Results are returned to the sponsoring agency and statistically analyzed. In a well-designed and controlled program, each laboratory should receive back the following information for each property tested: its day-to-day precision within the laboratory; the accuracy of the method used; its rank compared to other laboratories using the same methodology; the accuracy of its method compared to alternative methods; a statement of acceptability of the results (if norms for that technology have been established).

Through a survey of the more visible users and manufacturers of in situ instruments in the marine environment, an overview of current needs and practices for calibration and standardization evolved. Then through a field experiment the amount of error arising from these practices was demonstrated. In the following sections the current needs and practices are described in the context of the NBS recommendations.

CALIBRATION AND STANDARDIZATION TECHNIQUES

Definition of Terms

The terms "calibration" and "standardization" are widely used by a number of individuals often implying the same meaning. The differences however are significant. Calibration is the process of examining instrumental response to a series of prepared standards that bracket the expected concentration to be measured in the environment. The standards must be traceable, that is, of a certified concentration. Calibration must be performed at multiple points over the analyses range to adequately determine the instrumental response to the concentration change. Primary standards are directly traceable to a certified source such as the National Bureau of Standards. Secondary chemical standards may be prepared by dilution of a primary standard or prepared from reagent grade chemicals in the laboratory by the analyst. They are regarded as secondary standards because of the potential errors involved during preparation. The errors include: analytical balance accuracy and time since last inspection, purity and quality of the reagents, and the quality of the water used to prepare the solutions. Other variables include the cleanliness of the preparation area, type and condition of the mixing and storage container, stability of the solution, and human expertise.

Standardization is a procedure performed in the field that brings the instrumental response into the previously prepared calibration curve.

Generally, at least two points in the field should be taken with every profile or with 8-10 discrete measurements. This can only be accomplished when sampling from a sampler that houses the in situ probe and a series of water bottles. When an in situ measurement is taken, a water bottle must be signaled to collect a sample. This procedure will limit the variability resulting from spatial and temporal differences in the water column. Certainly, as R. A. Horne (4) points out in "Marine Chemistry," the sample will go through some changes as it is brought to the surface and the various gases in solution rearrange in proportions. The bottle composition and cleanliness must be controlled so as to not contaminate the sample. However, there is presently no other acceptable way of evaluating how effectively the in situ probe is operating in the environment. The differences tend to increase with the distance of the water column sample from the surface. For example, carbon dioxide is nearly twice as soluble at 1,000 meters as in surface waters. The concentration of carbon dioxide, of course, plays a significant role in determining the pH of the water.

The sensitivity of an instrumental measurement is defined as the change in signal or instrument output per unit change of concentration. The range of measurement is regarded as the span of concentrations in which the probe may be used to provide acceptable data within the stated performance specifications. The limit of detection is the lowest detectable signal which is normally equal to twice the ambient or normal background noise.

One-Point Calibration

A one-point calibration implies that the instrumental response is linear, can be internally normalized, or the slope of the response curve is linear over the measurement range. This assumption cannot be made unequivocally for all instruments under all conditions. In addition, care must be taken to insure that the response curve has not rotated around the calibration point. To justify one-point calibration, adequate field and laboratory data must be collected to verify that the response for the measurement type does not rotate or otherwise change under ambient conditions where problems are identified. A variety of corrective procedures may be carried out. As an example, consider the galvanic dissolved oxygen probe which must be calibrated using salinities similar to the salinity of the environment being measured. Calibration remains a particularly difficult problem where significant salt concentration gradients occur, such as between surface and deeper waters or in an estuarine stream where the salinity may range from less than 5 parts per thousand to 35 parts per thousand. While commercial probes have recently become available to compensate for this effect, it is not clear how well they actually operate. Additionally, the speed of water across the membrane may affect the metered response. Flow must be below the minimum level which distorts the membrane, yet above the level of stagnation. Because this effect (flow versus measured oxygen) plateaus, some instrument manufacturers have installed agitators near the probe surface to reach the effective speed where small changes in flow do not significantly alter response. Other physical variables which affect one point calibration for in situ instruments include the length of the cable between the probe and electronics packages, pressure, temperature, and trace inorganic constituents (i.e., sulfide).

The selection and use of a one-point calibration is not recommended

unless adequate field and laboratory data have been collected to support the linear curve assumption with full consideration of various field conditions, such as the effects of pressure, temperature, salinity, flow across the membrane, cable length, and concentrations of chemical constituents.

Recommended Means of Instrument Calibration and Standardization

All in situ marine measurements must be related directly to an accurate standard. The integrity or exact value of the standard must meet or exceed the level of accuracy achievable by the instrument and satisfy the program objectives. The National Bureau of Standards recommends a standards accuracy three times better than the user's required accuracy [Cali et al (3)]. There is limited value to water column profiling with an instrument which can only reflect relative rather than absolute values, particularly when most monitoring programs require several years worth of data to assess potential sublethal trend impacts which necessitate data inter-comparability. Data integrity derives from adequate documentation which traces instrument calibration with verified field standardization. The calibration and standardization procedures must be formalized and documented to spell out the approach, scope, and limits of in situ monitoring.

The documentation required includes the data of instrument calibration, type and integrity of standards, standardization values, and succeeding calibration results. Instrument repair and maintenance should also be documented. Ideally, instruments could be categorized in a manner that would indicate the type preferred for each application (e.g., deep sea) and for achievable levels of accuracies.

Documented calibration procedures should be required in every oceanographic program. Often when commercial firms are responding to a Government or industrial request for proposals that involve monitoring, price is a major award factor. As such, the low bidder may short cut data integrity in order to come up with the lowest price. The presence of a universally accepted and endorsed calibration and standardization procedure would close this obvious gap. Additionally, the procedures should be under yearly review to incorporate the most recent technology.

Training is a key element in performing the calibration. The procedures must be clear, concise, and supported with performance data and literature references. A variety of in situ instruments are available at different prices. Each has the manufacturer's suggested calibration procedures. This divergence and a lack of adequate documentation cause difficulty in training, with a consequent source of error in data comparability.

Standards used for calibration must serve a large community for a variety of needs ranging from compliance monitoring to the pure research scientist. They should be accessible to the analyst, relatively inexpensive, convenient to use, made of constituents which are stable over time, and of a certifiable concentration.

For each of the parameters under study, at least two levels of data quality assurance should be incorporated into marine in situ monitoring programs. First, instruments should be calibrated at several points over the

expected range of measurement, under conditions approximating critical environmental conditions, and with universally accepted standards. Second, in the field, samples should be collected in parallel with the in situ monitoring to verify instrument operation. Comparable techniques must be used for calibration and standardization. In the following sections, methods are presented.

Salinity--

Induction-type conductivity or salinity in situ probes, because of their size, are often very difficult for the user to calibrate. Usually manufacturers calibrate the units at their facilities prior to delivery and recommend return annually. The survey of users indicated that very rarely are the instruments returned unless a major repair is required.

A typical calibration procedure using the available standards is described. Briefly, a series of 200-liter tanks are prepared to contain a specific salinity water. A bench or laboratory salinometer, calibrated to Standard Seawater, is used to verify the salinity tank values. The in situ probe is then placed in each tank, and the values are recorded. A control sample of the water used to prepare the salinity tanks must also be analyzed. The accuracy of the method can be determined quite simply and is traceable back to a primary standard. The method is not without limitations. Ideally the laboratory salinometer should be calibrated with a primary standard at several points. However, at the present time, only one salinity standard is available (Standard Seawater). Also typical variations in environmental conditions, beyond pressure and temperature, should be incorporated into the calibration program.

Field standardization is required for data quality assurance. In the field, the analyst must collect discrete water samples at the probe during the time of measurement and analyze them by a reference method such as a laboratory salinometer. At least two samples should be collected with each profile or each daily use in the case of a fixed monitoring device. The analyses of these samples should be performed in real time while on station to verify calibration, otherwise whole sets of data might later be found unacceptable.

Standard Seawater is the only primary salinity or conductivity standard available to the analyst; it has a nominal salinity of 35 ppt. This standard has a reported accuracy of ±0.001 ppt, however systematic variations exceeding this level have been observed. The name "Eau de Mer Normale" was changed in 1960 to "Standard Seawater" and the name of the agency which distributes this standard was changed from "Depot d'Eau Normale" to "Standard Seawater Service."

The "Standard Seawater Service" is an agency under the "International Association of the Physical Sciences of the Ocean" (I.A.P.S.O.). "Standard Seawater" is certified in chlorinity only, but has been widely used as a standard for salinity determinations from conductivity measurements. Additional certified standards should be available at 10 ppt, 20 ppt, 30 ppt, and 40 ppt. These standards would limit the extrapolation errors in calibration. Pressure effects should be considered but they cannot be easily simulated at a low cost in the laboratory.

Temperature--

Temperature sensors should be routinely verified against an NBS calibrated platinum thermometer in the laboratory with a water bath accurate to 0.01°C. Currently both quartz and platinum reference thermometers are in use as standards, with the platinum predominating. An accuracy of .004°C is readily achievable according to NBS (5). Response should be checked at several points over the intended range of use.

In the field, standardization procedures can be performed with the aid of reversing thermometers mounted on the water bottles.

Dissolved Oxygen--

The conventional method of in situ dissolved oxygen probe calibration is the modified Winkler titration. Air-saturated seawater at room temperature is typically measured with the probe, and then by the Winkler and by adjustments made to the instruments. Some analysts check the probe response to zero by immersing the unit in a solution to which a small amount of sodium sulfite crystals has been added, or in seawater purged with nitrogen gas. A micro burette procedure using dilute reagents delivers exceptional accuracy. Typically in situ dissolved oxygen instruments are calibrated at one point in the field. No chemically certified standard is produced or available in the United States for dissolved oxygen calibration. Recommendations have been made for a physical standard preparation. This procedure would involve purging a seawater solution with various proportions of atmospheric air and nitrogen gas to provide incremental solutions to saturation. The actual concentration of the standards may be determined by the modified Winkler method or by other conventional methods such as gas chromatography (J. Sullivan, NOAA/NOS pers. comm.) or colorimetry. However, these methods are time consuming and require more expensive instrumentation.

In the field, standardization must be determined by simultaneous collection of discrete water samples at the probe using a rosette or other multiple sampling device.

pH--

pH buffers are available from a variety of commercial manufacturers or may be prepared by the analyst according to NBS specifications. Whatever the case, pH meters must be laboratory calibrated at several values over the range of use, and standardized at a minimum of two points. The narrow range of pH values in ocean waters enhances the ability to calibrate instruments properly.

For field standardization, a discrete water sample from a water bottle located adjacent to the probe must be collected.

ACCURACY AND RELIABILITY

Replication Error

Replication errors are observed when different values are measured for a known homogenous environment. However, replication problems may occur if the water sample collected in the environment is from a different point in time or different water mass. In situ probes must be carefully calibrated to

achieve the stated accuracy of the manufacturer. Typically, manufacturers quote precision-accuracy figures for their instruments which often differ from the analytic figures. Also, the operator tends to read the meter value as an absolute value. If a manufacturer's specifications for a dissolved oxygen unit are ±0.1 ppm, the user should only record the display value to this significant figure. However, the analyst may ascribe an accuracy to the measurement which cannot be verified by the analytic technique.

TABLE 1. REPRESENTATIVE INSTRUMENTAL CAPABILITIES
DATA FROM MANUFACTURERS SPECIFICATION SHEET

Parameter Manufacturer (Model No.)	Accuracy	Precision	Range
Dissolved Oxygen			
Plessey (9050)	±0.15 ppm	±0.10 ppm	0 to 15 ppm
YSI (Model 57)	NA	±0.10 ppm	0 to 25 ppm
Montedoro-Whitney (Dor-1B)	±0.10 ppm	NA	0 to 10 ppm
	±0.20 ppm	NA	0 to 20 ppm
Ocean Data	NA	±0.20 ppm	0 to 20 ppm
Salinity			
Plessey (9050)	±0.02 ppt	±0.003 ppt	30 to 40 ppt
YSI (33)	±0.9 ppt at 40 ppt; ±0.7 ppt at 20 ppt	NA	0 to 40 ppt
Temperature			
Plessey (9050)	±0.02°C	±0.004°C	-2 to 35°C
Plessey (4005)	NA	±0.50°C	-2 to 35°C
YSI (Model 33)	NA	±0.1°C at -2°C; ±0.6°C at 45°C	-2 to 50°C
Montedoro-Whitney (MK III A/B)	NA	±0.03°C	-5 to 45°C
Ocean Data	NA	±0.1°C	-5 to 40°C
pH			
Plessey (4005)	NA	±0.02 pH units	2 to 14 pH units
Montedoro (DPH-1B)	±0.005 pH units	NA	0 to 14 pH units
Ocean Data	NA	±0.1 pH units	0 to 14 pH units

NA - Not Available

The accuracy and precision typically reported by manufacturers, based on instrumental capabilities for dissolved oxygen, range in accuracy from 0.1 to 0.2 ppm and from ±0.1 to ±0.2 ppm in precision. The applicable measurement range is commonly from 0 to 20 ppm. Salinity probes typically have a reported accuracy ranging from 0.02 to 0.9 ppt, with a precision of ±0.003 ppt. The greater accuracy range is available with an instrument of 30 to 40 ppt range. Temperature units have an accuracy of 0.02 to 0.1°C, with a precision ranging from ±0.004 to ±0.1°C over a usual range of -2 to 35°C. pH probes generally have a precision of ±0.02 to ±0.1 pH units over the range of 2 to 14 pH units. The instrumental capabilities of representative in situ instrumentation are summarized in Table 1.

Analytical Error in Calibration

The accuracy of standards can only be verified by the best analytical techniques. The technique must be relatively simple, and should be low cost and relatively quick to perform. The modified Winkler as it appears in Strickland and Parsons (6) has a reported precision of ±0.079 ppm over the range of 0.081 ppm to super saturation. pH standards are available to four significant figures through NBS, while the Environmental Protection Agency (7) lists a precision of ±0.1 pH units. Salinity as performed by the wet chemical method in Strickland and Parsons (6) offers the analyst two ranges from 4 to 40 ppt, with a precision of ±0.06 ppt at 30 ppt or 30 to 40 ppt with a precision of ±0.023 ppt at 33 ppt. The end point may best be determined by the conductivity titration method. Temperature may be measured with NBS calibrated quartz thermometers to an accuracy of 0.02°C over a very wide range. The representative analytic techniques for calibration are listed by parameter with precision and range data in Table 2; Table 3 lists the common standards used for calibration.

TABLE 2. REPRESENTATIVE ANALYTIC CAPABILITIES

Parameter/Source	Precision	Range
Dissolved Oxygen		
Strickland & Parsons (1972)	±0.079 ppm	0.081 - 12.96 ppm
Environmental Protection Agency (1974)	±0.20 at 7.5 ppm	NA
pH		
EPA	±0.1 at 3.5 pH units ±0.12 at 7.7 pH units ±0.12 at 8.0 pH units	0 - 14 pH units
Salinity		
Strickland & Parsons (1972)	±0.06 ppt at 30 ppt ±0.023 ppt at 33 ppt	4 to 40 ppt 30 to 40 ppt

NA - Not Available

TABLE 3. COMMON STANDARDS FOR CALIBRATION

Parameter	Accepted Standard	Conc./ Accuracy	Applicable to In Situ Calibration	Several Point Cal.
Salinity (through conductivity)	Standard Seawater	35 ppt (nominal)*	No	No
Dissolved Oxygen	Winkler - Mod. Azide	Variable	No	Variable
pH	NBS Buffers	3.557**	No	Yes
	NBS Buffers	4.004**	No	Yes
	NBS Buffers	6.863**	No	Yes
	NBS Buffers	7.415**	No	Yes
	NBS Buffers	7.669**	No	Yes
	NBS Buffers	9.183**	No	Yes
	NBS Buffers	10.014**	No	Yes
Temperature	National Bureau of Standards Quartz Calibration Thermometer	-80 to 250°C/ ±0.002°C	Yes with water bath	Yes

*at 15°C and 1 atmos. with batch-to-batch variations as high as 0.01 ppt; within batch variation of 0.001 ppt.
**uncertainty of ±0.005 at 25°C.

ALTERNATE CALIBRATION TECHNIQUES

Temperature

The options open to the analyst for temperature sensor calibration are few. All that can be determined by calibration is that the sensor is responding accurately. The type of water bath used is not critical but should be calibrated against a recently checked NBS standard thermometer which is accurate to at least the level of probe accuracy required.

Salinity

Salinity standards may be prepared in the analytical chemical laboratory from a synthetic seawater mixture or with the proper proportions of at least reagent-grade chemicals. However, because of the number of variables involved (i.e., micro-balance accuracy, age and conditions purity of the reagents, analytical techniques, and the quality of the water used to prepare the solutions), the accuracy of the final solutions cannot be assured beyond two to three significant figures.

Dissolved Oxygen

A technique some manufacturers recommend for dissolved oxygen probe calibration is to wave the probe in the air. The meter value should correspond to a chart value taking into account the barometric pressure and temperature. Frequently these data are not sufficient for statistical treatment but adequately demonstrate that the readings did not correspond to the Winkler values when the probe was calibrated by waving it in air. This method is not a preferred technique for one-point calibration or standardization. Discussions with NOAA personnel indicate that it is not possible to obtain reproducible results.

pH

The analyst may prepare his own standards from the analytical chemical laboratory, reagent-grade chemicals. This option is also not recommended for reasons outlined in the salinity discussion.

MEASUREMENT DEGRADATION

Measurement degradation cannot be easily determined without standardization. The accuracy and precision of a unit can only be evaluated by comparison with a standard reference technique. For this reason calibration with standardization is essential to collect meaningful data.

Most in situ instruments automatically check for proper electronic operation but have no means for determining the condition of the sensor. This obvious disadvantage must be confronted in future design efforts.

The variance as a result of instrument degradation is presently undefinable, but could be resolved by repetitive calibration. Sensors may slowly degrade until the malfunction is obvious. The period between new part installation and degradation is a wide band where several errors may occur. Cleaning, replacement, and other activities affect probe calibration, sensitivity, and accuracy. While these activities are required, frequent calibration and standardization are essential to detect when measurements begin to diverge systematically from the calibrated accuracy.

SECTION 5

REFERENCE STANDARD REQUIREMENTS FOR CHEMICAL IN SITU INSTRUMENTATION

REFERENCE STANDARDS FOR CURRENTLY MEASURED PARAMETERS

The evaluation of standards for in situ measurements must be related to the present instrument accuracy and precision capabilities. Ideally, the standard reference material should be more accurate than the probe, which would allow for instrument improvement with time. Allowances for variations in instrument capabilities and the user's requirements should also be made.

Sensitivity

The sensitivity of in situ probes to changes in concentration of dissolved oxygen and salinity is reportedly less than the manufacturer's stated overall accuracy. Only pH sensors are more sensitive than required by both research and survey groups. Clearly, care should be used in reporting data to the correct degree of precision. As an example, a conductivity probe with a sensitivity of only 0.25 mS/cm used with an instrument having a stated accuracy of 0.10 mS/cm is not providing data to the stated accuracy of the instrument.

Probes are not totally selective for one parameter. Dissolved oxygen probes respond to such energy sources as light and water movement. Various ions present in seawater may produce a response in the probe. (J.H. Carpenter, University of Miami, pers. comm.).

Limit Of Detection For Parameters Now Measured

The normal oceanic range of values of temperature, salinity, dissolved oxygen, and pH are found in Table 4.

TABLE 4. RANGES OF COMMON OCEANIC PARAMETERS

	Temperature (°C)	Salinity (ppt)	Conductivity (mS/cm)	Dissolved Oxygen ppm	pH (Units)
Minimum	-2	20	17	0	7.7
Maximum	+30	40	60	15	8.5

Interferences Associated With Parameters Now Measured

Temperature--

Temperature probes are generally stable under environmental conditions and are considered reliably accurate for up to 6 months of in situ use (8).

Conductivity--

Conductivity may be measured by seawater-coupled transformers or electrode devices; however, electrode devices are easily fouled, polarized, and corroded in seawater and are seldom used. Conductivity cells are still subject to hysteresis effects, and techniques using STD and CTD devices should be rigidly controlled to minimize this problem.

Salinity--

Salinity measurements in situ are conversions by electronics circuits of conductivity and temperature sensors. Lack of linearity and inability to perform the necessary complex calculations reduce accuracy. Digital electronics may reduce the analog errors now present.

Dissolved Oxygen--

Membrane electrodes used to measure oxygen have a very slow response time. Nonmembrane (naked) electrodes are sensitive to hydrodynamic properties of the environment and are easily fouled. Compensation for temperature and pressure effects has been successfully applied to depths of 3,000 meters (9).

pH--

pH system nonlinearity is commonly caused by reference electrode malfunctions and drift (10). Although this is not large in laboratory tests (0.003 pH in 24 hours), it is commonly severe in field instruments due to fouling of the glass membrane after about 24 hours of use (11). Another problem is with cracks in the reference cells which frequently are not detected with a one-point calibration.

Accuracy For Parameters Now Measured

Accuracy, as used here, refers to how closely a set of measurements cluster about a chosen reference standard value, and as such includes random and systematic errors. The accuracy of an in situ measurement system depends on the integrated functioning of its components, including the operator, under field conditions. Although often reported, laboratory accuracies of equipment designed to operate in situ are not adequate descriptions of instrument accuracy. In tracing a measurement from the field environment through the measurement device to the final recorded value, a number of possible errors are encountered.

First is the error due to inexact correspondence between the probe's response and the ambient condition; this is called sensitivity. The response in the probe must then be translated into an electric potential which is transmitted to a measuring device. The error in this step is called probe accuracy.

The electrical and electronic instability of the device results in two additional errors. The first error is more or less random over a long period

of time and is referred to as repeatability. The second is vectored over time and is usually measured as 24-hour stability, or drift. The display of the measured value results in the error called readability. Manufacturers often lump these errors in a total instrument accuracy value, which may or may not reflect the greater portion of the actual system accuracy.

In addition to the errors accumulated when making a measurement under controlled conditions, in situ instruments are variously affected by pressure, temperature, and other physical and chemical conditions present in the environment. Compensation for environmental conditions may be built into the instrument or, as in the GEOSECS program, it may be desirable to correct raw measures by means of shipboard or laboratory computer systems. The error due to inexact compensation for environmental conditions should be considered when reporting total accuracy.

Platinum temperature transducers have a representative overall accuracy of ±0.01 percent. Reversing thermometers have an overall accuracy of about ±0.02°C. Inductively coupled transformers for salinity measurements have a transfer function accuracy of about ±0.02 ppt. Dissolved oxygen electrodes have a reported accuracy of ±1 percent (±0.1 ppm) as stated in manufacturers' literature.

The International Biophysics Corporation reported the problem of interpreting manufacturers' stated accuracies for dissolved oxygen. "It is our opinion that, with the present state-of-the-art of dissolved oxygen measurement, it is impossible for most manufacturers to meet their stated accuracy specifications across the entire dissolved oxygen and temperature ranges."(12)

Temperature transducers now used for oceanographic purposes introduce errors due to nonlinearity, stability, response time, usable life, and maintenance. Platinum thermometers can be obtained with a drift of only 0.011°C over 6 months (8). Copper and platinum thermometers have a linearity of ±0.01°C from -2°C to +20°C using the Callender-Van Dusen equation (5).

Temperature thermistors of the oxide type exhibit an aging effect and an increase in resistance with time. About 0.5 to 1.5% of the resistance variation occurs within the first week of use. Changes of 1% may still occur after several months of use. Exposure of the thermistor to a temperature slightly higher than that to which it will be subjected (in a process also called aging) may reduce drift to as little as 0.04% per year (8). Since thermistors are nonlinear, best least-square fits with third- or fourth-degree polynomials yield a temperature compensation of no better than ±0.01°C (8). A three thermistor compensation network has shown an actual linearity of only ±0.04°C.

EXTENSION OF IN SITU INSTRUMENTS TO PARAMETERS NOT NOW MEASURED

Reference standard requirements should be established for parameters not now measured. Manufacturers and researchers are currently developing a wide range of instruments designed for in situ use. Reference standard development should proceed in parallel with in situ instrument development to assure data accuracy and reliability.

Currently, 19 parameters are measured in situ and other parameters (Table

5) are under consideration for application to seawater. Studies of stability and accuracy have begun for some of the specific ion electrodes. It is difficult to predict the future acceptance for routine application of any system. However, the rate of growth of human impact on the environment will encourage more continuous monitoring of parameters. Parameters of more imminent concern might be identified from review of the environmental problems under study and the parameters of concern to the studies. Heavy metals should be a leading contender for in situ measurement. Cadmium, mercury, and lead are among the more important. Vanadium has been found to be associated with the heavy fractions of petroleum.

TABLE 5. PARAMETERS MEASURED IN SITU

Presently Measured

Calcium	Magnesium
Chloride	Oxidation-Reduction Potential
Chlorophyll	pH
Conductivity, electrical	Potassium
Dissolved oxygen	Rhodamine-B (flushing studies)
Fluoride	Salinity
Fluorescein (flushing studies)	Sodium
Hydrocarbons	Temperature
Light attenuation	Transmittance, optical
	Turbidity

Possible Future Application

Aluminum	Chromium
Ammonia	Cobalt
Antimony	Copper
Arsenic	Dysprosium
Barium	Europium
Bromine	Fish "species" density
Cadmium	Fluorine
Calcium	Gallium
Carbon dioxide	Germanium
Cesium	Gold
Chlorine	Indium

continued

TABLE 5. (continued)

Possible Future Application	
Iodine	Potassium
Iron	Selenium
Lithium	Silicates
Lawrencium	Silver
Lead	Sodium
Magnesium	Strontium
Mercury	Sulfide
Molybdenum	Sulfur
Neodymium	Tin
Nickel	Titanium
Niobium	Tungsten
Nitrate-Nitrogen	Total Kjeldahl nitrogen
Nitrite-Nitrogen	Total Phosphorus
Reactive phosphate	Uranium 238
Osmium	Vanadium
Particulate matter	Yttrium
Plankton "species" density	Zinc
Platinum	Zirconium

SURVEY OF NATIONAL ACCURACY REQUIREMENTS

For the purposes of this study, manufacturers and instrument users were contacted in the United States. Also, users from Japan, West Germany, the Soviet Union, France, Poland, Australia, the United Kingdom, and Kenya were contacted. A limited field survey of operational in situ equipment calibration and standardization techniques, as well as present and desired levels of accuracy, was conducted. Individuals contacted were involved in major marine sampling programs, including the Coastal Upwelling Experiment (CUE), the California Cooperative Fisheries Investigation (CalCOFI), the North Pacific Experiment (NORPAX), Geology-Chemical Sections (GEOSECS), Outer Continental Shelf (OCS), and the Dredge Material Research Program (DMRP). These programs represent sponsorship by the Bureau of Land Management, the U.S. Army Corps of Engineers, the Environmental Protection Agency, the National Science Foundation, and the National Oceanic and Atmospheric Administration, which includes the National Marine Fisheries Service. While it is not an exhaustive review of the practitioners, it accomplishes the intended purpose of indicating the current practices and establishing the scale of accuracies sought by major users. The survey included 60 individuals representing 10 institutions operating within 8 major programs under 6 sponsors. Additional information was gathered from the industrial and scientific literature.

U.S. Government research and funding agencies such as the Department of Commerce's National Oceanic and Atmospheric Administration; the Environmental Protection Agency; the Department of the Interior's Fish and Wildlife Service, Bureau of Land Management, and Geological Survey; the U.S. Army Corps of Engineers; and the National Science Foundation routinely support water quality measurements with in situ sensors.

State and local environmental monitoring agencies often acquiesce to specifications of U.S. Government agencies; some establish their own accuracy specifications for water quality. Some of these local government programs have grown in scope and have eclipsed the more widely known national program.

A wide range of international programs are under way with still another specification of accuracy. The most common in situ measurements among all users are temperature, electrical conductivity, pH, dissolved oxygen, and pressure (or depth). A summary of the accuracy requirements for these parameters (except depth) among research and environmental survey groups is given in Table 6. As part of the teaching program, schools and other groups often perform cursory surveys which include measurements on the parameters under study. These measurements will sometimes find their way into public archives, although such accessory measurements are often considerably less accurate than those required by research and survey groups. Survey requirements correspond closely with manufacturers' stated best accuracies. Frequently, researchers require more accuracy (except for salinity) than possible with commerical equipment. For both groups, the observed accuracy reported for dissolved oxygen is considerably less than the desired accuracy. In summary, the survey revealed:

- For the most part, instruments in present use have been used for several years or more. Reliability is generally conceded as good for all but one CTD unit at the University of Washington which was a relatively early model.

- No one expressed much enthusiasm over future prospects to develop sensors for additional parameters or for refining those sensors presently available. The need for more accuracy and finer resolution was recognized by two or three individuals but not to the extent that they would promote such an undertaking. The problem arises from the very low concentrations found for most environmental parameters and the high noise band likely to surround the measurement itself.

- Approximately the same attitude, that little benefit would be gained, persisted in answer to the question of improvements in calibration and standardization. The parties recognizing the need for standards were survey or monitoring groups, whereas research groups were concerned with instrument capabilities.

- While it cannot be quantified, it seems as if those individuals using the in situ instrumentation in long-term monitoring are able to operate with less exacting equipment and are more concerned with standardization between installations. By contrast those in the experimental group seek

exact data and are satisfied to assure their values within their own experimental "structure." This "structure" may include one investigator, a department, or a program.

TABLE 6. ESTIMATES OF BEST OCEANIC IN SITU ACCURACIES

	Temperature (°C)	Dissolved Oxygen (ppm)	Salinity (ppt)	pH (units)
Error Sources				
Probe Sensitivity	0.01	0.25	0.25	0.0025
Probe Accuracy	0.015	0.1	0.30	0.004
Repeatability	0.01	0.1	0.003	0.001
Readability	0.01	0.05	0.002	0.01
In Situ Errors				
Drift (24 hour)	0.5	-	-	0.003
Temp. Compensation	0.01	0.008	0.33	0.02
Pressure Compensation (10,000 m)	0.81	-	-	-
Water Agitation Error	-	0.05	-	-
Manufacturer Stated Accuracy	0.02	0.01	0.02	0.01
Research Observed	0.01	0.5	0.30	0.10
Required Accuracies				
Research	0.01	0.01	0.03	0.02
Survey	0.05	0.1	0.03	0.5
Accessory	1.0	1.0	0.5	0.5

INSTRUMENTATION

Frequency of Standardization Required

The majority of users were found to use Standard Seawater only when calibrating by an automated laboratory salinometer. The standardization procedure is only carried out a few times during an experiment, or once in several months. Errors from instrument drift, degradation, fouling, and reliability indicate standardization should be carried out frequently.

Cross checking between two instruments provides a partial quality check on resulting values (J.H. Carpenter, University of Miami and K. Grasshoff,

University of Kiel, pers. comm.). Cross checking of discrete samples against a continuous profiler generally cannot be used to verify more than a few percent of continuous monitoring data, but should be used in conjunction with in situ instruments no less frequently than once in every profile, or every few days for non-mobile instrument packages (A. Bainbridge, GEOSEC, pers. comm.).

Present Uncertainty In Instrument Measurements

An attempt to quantify an estimate of uncertainty in instrumental measurements was terminated when the review of user practices disclosed a lack of traceability to a common reference material or reference method. Quantitative values of percent uncertainty should be estimated as average percent deviation from the known mean. Percent error of the measurement is determined by attempting to repeat a single measurement many times on a parameter of known value. The spread of the data points estimates this error. In lieu of quantification, a discussion of the sources of uncertainty and the potential quantifiable uncertainty as a function of the standards available is provided.

Manufacturers' Standardization Procedures--

Nonlinearity of an instrument results in a curve when data points derived from that instrument are plotted against the actual values. This in itself does not constitute an error. However, when converting the instrument output to standard units of measure some error is produced. This error is measured by the magnitude of difference between the resulting converted measure value and the actual value. It should be noted that simplistic analog conversions within the instruments are often considerably nonlinear with a resulting large conversion error. For this reason GEOSEC has removed analog conversions from their oxygen meters and are using ship-board computer conversions. The GEOSEC technique is a considerable improvement over commonly used techniques, although some researchers do not consider the shipboard routine conversion to fully meet their standards.

Temperature--Manufacturers of CTD's and STD's recommend the system be returned to their lab approximately once per year for calibration. The CTD or STD is placed in a constant temperature-salinity water bath (verified by NBS methods), and the thermistor and conductivity cell are then adjusted. NBS has a standard adequate for calibrating temperature sensors.

Salinity--I.A.P.S.O. Standard Seawater is the standard reference for calibration of both in situ and laboratory salinometers. It is in routine use in the oceanographic community and is the salinity reference. It is considered difficult to duplicate the solution in the laboratory. Currently, Standard Seawater is being distributed by the Institute of Oceanographic Sciences in Surrey, England. This standard solution has a certified uncertainty of ±0.001 ppt chlorinity. Calibration to the standard using potassium chloride techniques has a reported uncertainty maximum of ±0.01 ppt salinity. The best American refractometers have a reported accuracy of ±0.05 ppt salinity; however, a Russian interferometer system has a reported accuracy of ±0.01 ppt salinity.

Dissolved oxygen-- Sagami Standard Seawater Reference Solution Source prepares and distributes worldwide CSK standard seawater reference solutions, including one for dissolved oxygen. The solution is used without dilution,

and the colorimeter technique is based on a standard color development to calibrate absorbance in a spectrophotometer. In general, the Sagami samples are designed to remain stable for at least 1 year after preparation. The most widely used dissolved oxygen reference standard worldwide are modifications of the Winkler procedure.

Calibration of dissolved oxygen probes often uses air saturated water as a standard. The maximum accuracy of this technique is 0.1 percent, due to problems with variations in air quality and supersaturation at low temperatures encountered in the field (13).

pH--Standard pH buffer solutions are prepared by many chemical and manufacturing companies to the exact formulas prescribed by the National Bureau of Standards. The certified accuracy of these standards is ±0.01 pH units. There is good reason to conduct seawater sensor calibration at something greater than a pH value of 7.0. Testing at a pH of 8.0 rather than 7.0 has an immediate advantage of being closer to the seawater average of pH 8.0 to 8.3.

Buffer solutions are less stable than powder buffers. Solutions in storage are stable up to a year, whereas buffer powder or buffer tablets can be stored indefinitely. However, with buffer powders, the mixing methods in the field must be as accurate as normal analytical methods followed in an equipped chemistry laboratory.

Instrument standardization to a pH buffer standard has a maximum reported accuracy of ±0.02 pH units at 25°C as measured with a precision pH meter. Problems of comparing standard pH buffer solutions to measurements in seawater result in an additional error due to interferences that should be solved by setting up rigid standards for seawater buffer solutions and standardization methodology.

Users' calibration and standardization--Users often choose different standards since a common standard is not recognized for most of the parameters. The procedure for calibration standardization is produced from manufacturers' instructions, laboratory manuals, research journals, and text books, or are invented to meet the user's specific needs. Considering these circumstances, comparison of data between independent researchers is questionable. The need for comparable water quality measurements necessitates the development of reproducible standard analytical techniques.

Users introduce four additional errors into the measurement process. Without proper control of these errors, data cannot be considered standardized.

- Procedures may be modified by a laboratory to meet their needs. Such modifications change the procedural error and are referred to as procedural modification errors.

- Human errors are procedural errors resulting from the measurement being taken by different operators.

- Training error results when operators of different levels of learning make the measurement.

°Technology errors result when new instruments are developed. The spread of data points due to different instruments making the same measurement estimates this error. It is necessary to subtract from this value instrument error, standardization error, and, if necessary, operator error, as well as sampling error to obtain the actual value.

The necessity of using rigid procedures during calibration, standardization, and measurement is stressed. The inaccuracies resulting from inadequately trained personnel following many manufacturers' techniques are documented by the cruise results (Appendix B). Improved procedures, such as are documented in the CalCOFI/GEOSECS procedures manuals, should be used at all times. (Note: Errors may still arise from other facets of sampling design.)

The GEOSECS program determined that calibration of equipment at excessively short intervals actually resulted in a degradation in overall accuracy. If the instrument can be determined to have a known bias, the data can be readily corrected by computer programming or manual data correction.

°Temperature sensors usually must be calibrated by the manufacturer, while most users are only able to make a few crude comparisons (±0.1°C) to a laboratory thermometer.

°CTD and STD systems are usually field standardized by simultaneously profiling and collecting discrete water samples, then comparing the CTD or STD temperature and salinity data with measurements of the water samples taken by reversing thermometers and laboratory salinometer.

°For salinity and pH, the user will make dilutions of the standard solution to obtain a set of working standards to calibrate the sensor or probe. Ideally, the sample value will fall within the range of the working standards. The user often prepares his own standards by dissolving reagent grade (99% or greater purity) salts into distilled de-ionized water. To eliminate the matrix effect, an ionic strength buffer should be added to the standard solution. The standard method of calibrating in situ salinity instrumentation is by the laboratory salinometer method. The standard instrument for salinity measurements is considered to be the high accuracy-precision laboratory salinometer. This type of salinometer uses the inductive coupling technique to measure conductivity and is automatically temperature- and pressure-compensated.

°Dissolved oxygen sensors can be coarsely standardized with air-saturated seawater. If the temperature of the water is known, solubility tables will provide an "accurate" value of the percent saturation.

In situ dissolved oxygen measurements are usually calibrated against the standard Winkler method performed on water bottle samples. Calibration is performed using distilled water for freshwater work. Even though bottle samples are not exactly comparable to in situ measurements, in situ measurements are often terminated when discrepancies are found between reversing thermometer or water bottle sample values and in situ values (A. Bainbridge, GEOSECS, pers. comm.). Some users cross-calibrate between two in situ systems without close calibration to any outside standard. The University of Miami recalibrates both in situ systems if a difference of greater than 0.1 ppm of

oxygen is found (J. Carpenter, University of Miami, pers. comm.).

Cruise Reports

The at-sea operation was carried out April 13, 1977, to further study the problem of standardization and calibration technqiues, and to determine the comparability of measurements obtained using the calibration and standardization techniques recommended by equipment manufacturers. The at-sea operation utilized electronic in situ instrumentation systems and standard sampling techniques for dissolved oxygen, pH, temperature, and salinity. The survey was conducted at five stations in Monterey Bay, California. Temperature, salinity, dissolved oxygen, and pH were measured at the surface, and at depths of 5, 10, 20, 30, 40, and 50 meters (Appendix B).

Calibration of the equipment prior to the cruise was performed according to manufacturers' specified procedures: dissolved oxygen was calibrated against air-saturated seawater; conductivity with Standard Seawater; pH by standard NBS buffer solutions; and temperature probes by the constant temperature bath method in comparison with a platinum thermometer. The instrument systems were under manufacturers' calibration. A representative of LFE participated in the cruise procedures along with Interstate Electronics Corporation personnel. Four in situ systems were tested: Horiba, Hydrolab, Martek, and Plessey Environmental Systems. All four parameters were measured by the Horiba, Hydrolab, and Martek systems; the Plessey system did not measure pH and dissolved oxygen.

In addition to the in situ instruments, a Beckman (RS7C) Laboratory Salinometer was used to measure conductivity, Winkler titrations were used to measure dissolved oxygen, and a reversing thermometer was used to measure temperature. These methods were used as checks on the in situ instrument performance. Conductivity measurements were performed by inductive coupling and multiple electrode sensors (from which conductivity ratios were determined and subsequently converted by use of tables). Dissolved oxygen was measured by membrane polarographic electrodes; pH was measured by glass electrodes; and the temperature sensors were resistance transducers. All instruments were capable of measuring the oceanic range of each parameter. All water samples were collected with standard Nansen bottles. Depth was calculated by triangulation when necessary after measuring the wire angle.

Statistical methods--

The 95% confidence interval was calculated on each system for each parameter as a measure of the accuracy of the method employed. The confidence intervals were calculated using the method given by J. Freund (14) for small samples. The sample variance was estimated for each system as the sum of the squared deviations from the calibration procedure. The following procedures were assumed to be calibration procedures:

Winkler method:	dissolved oxygen
Calibrated reversing thermometer:	temperature
Beckman laboratory salinometer:	salinity
Statistical mean pH value:	pH

The mean square differences were calculated between the in situ method and the calibration method by the paired value method to eliminate distribution dependency and the effects of depth and location (15). Tests for significant differences between techniques were performed by means of the small sample paired t-test for comparing a sample mean to a theoretical mean (14).

This total interval may be partitioned into the uncertainty caused by the analytical method (precision) and the uncertainty attributable to systematic error (calibration). Partitioning of the interval into two t-statistic intervals (precision and systematic) is shown in Table 7.

TABLE 7. PARTITIONED STANDARD DEVIATIONS FROM INTERCOMPARISON EXPERIMENT

Parameter	Methodology	Systematic	Total
Temperature	0.010	0.18	0.28
Salinity	0.102	0.470	0.572
Dissolved oxygen	0.175	1.007	1.182
pH	0.113	0.365	0.478

Cruise observation results--

Considerable differences were found between the values reported by the various in situ instruments. Only one temperature system, two dissolved oxygen systems, and one pH system demonstrated a lack of significant difference from the chosen calibration system (Table 8).

Sampling was inadequate to determine behavior of the measurements due to pressure differences. Statistical interpretation is also limited by the lack of replication. Even under the best of circumstances, it is essentially impossible to obtain a true replicate measure in such a heterogenous environment. Since all measurements were made during a 10-hour cruise, no discussion of drift, marine biofouling, durability, or reliability is warranted.

All parameters showed a greater standard deviation due to systematic error than to methodology (Table 7). This suggests considerable calibration error, and points out the problem of independent calibration of systems by manufacturers and the nonequivalency of calibration techniques used for different instruments.

It is suspected that part of the error between methods could be reduced by a uniform calibration procedure. No single procedure was devised that could accommodate the differences in equipment structure. Ship-environment interaction, such as bilge effluent, propwash, and engine cooling effluent, was a potential problem. Precautions were taken to avoid such problems, and the data did not reflect these influences (increased standard deviation values of surface water quality measurement).

Depth compensation requires an accurate measurement of pressure. Two systems incorporated pressure transducers in their in situ systems. The other systems used cable length markings and triangulation (when wire angle was greater than 5°) to estimate depth. One system uses the bonded strain gage, which is considered a very accurate method of determining depth (8). This transducer is automatically temperature-compensated; accurate compensation is important since gage impedance varies significantly with temperature (8). No comparison between cable lengths, pressure transducers, or triangulation techniques was attempted. Fortunately, since wire angles were slight on this particular cruise, the inaccuracy of depth measurements was not considered a major problem. In rougher seas, the cable length and triangulation method of depth estimation is much less accurate than a pressure transducer. Placement of more weight in the sonde would improve some of the systems environmental applicability. The sonde unit is very light and easily responds to ship movement and currents. This is a very undesirable characteristic as water depth uncertainty becomes a problem.

TABLE 8. 95% CONFIDENCE INTERVALS WITH PAIRED T-TESTS FOR SIGNIFICANT DIFFERENCES BETWEEN SAMPLE AND CALIBRATION MEASURES

Parameter	System	n	95% C.I.	Std. Error	Probability of Difference from Standard
Temperature	A	13	0.171	0.097	3.38*
	B	24	0.103	0.050	4.22*
	H	18	0.115	0.055	3.27*
	C	24	0.196	0.095	4.29*
	D	20	0.111	0.053	2.67
Salinity	A	11	9.02	4.049	3.28*
	B	25	0.127	0.061	4.82*
	H	19	3.28	1.489	4.35*
	D	22	0.016	0.008	3.56*
Dissolved Oxygen	C	25	0.374	0.183	3.91*
	B	24	0.525	0.508	2.12
	A	11	1.69	0.816	0.64
pH	G	24	0.07	0.008	16.0*
	A	13	0.03	0.015	2.72
	B	23	0.04	0.018	3.21*
	H	19	0.05	0.023	3.43*

* = 99% probability of a difference
(* = significance level of better than 0.01)

Temperature--The 95% confidence interval covers 2.8% of the average sample mean, or ±0.28°C. One was consistently high, recording values outside

the confidence interval 69% of the time. All the values recorded by another system were lower than the sample mean (by an average of 3%) and outside the confidence interval in 48% of all measurements. This consistently large range between systems suggests calibration (systematic) error.

The reversing thermometer and only one thermistor system showed close agreement at all stations and depths. The response time for all systems varied between 30 and 60 seconds. During the cruise, all the temperature measuring systems operated properly, and no repairs or replacements were necessary. All systems were reliable, relatively sensitive, and had a short response time. Previous studies yielded similar results (8).

The reading uncertainty standard deviation for one system was ±0.16°C, which is 0.10°C greater than the uncertainty reported by NOIC Instrument Fact Sheet #75004. The uncertainty for another system was ±.09°C, which is 0.08°C greater than the uncertainty reported by NOIC Instrument Fact Sheet #76012.

Salinity/conductivity--Previous CalCOFI studies have determined that the expected salinity range of Monterey Bay is 33.0 to 34.0 ppt for the summer months. Since values from two systems were far outside this range, these values were not included in the sample mean and confidence interval calculations. One system reported values of about 18.8 ppt, and the other system about 27.3 ppt. The 95% confidence interval calculated from readings of the remaining three systems was ±0.57 ppt, or approximately ±1.5% of the sample mean.

Two systems showed significant agreement at all stations and depths. Both systems recorded salinities lower than a third system; however, reported values were six and five significant figures, while the third gave three significant figures. This difference in data reporting with the resulting recording errors could partially account for the range between salinity values.

Conductivity is a function of salinity, temperature, and pressure. Therefore to achieve accurate conductivity values, precise measurement of these three parameters is essential. Compensation for temperature and pressure variations is included in all salinity data presentations. All salinity recording systems compared in this study measured conductivity. Two systems used inductive coupling techniques, and the others used multiple electrodes.

Polarization could have been a problem since all instruments used less than the recommended 1 KHz power source (8). Response time varied between 1 and 3 minutes for all systems. Mechanically the five systems were reliable, excepting the gross errors in two of the systems.

Dissolved oxygen--The 95% confidence interval for dissolved oxygen is ±1.18 ppm, or approximately ±15% of the sample mean. The wide range of values reported for the same sample yields a relatively large confidence interval, often as large as 15-20% of the sample mean. No two systems agreed more closely than 0.2 ppm.

During the measurement of dissolved oxygen, the expected sample collection problems were accompanied by a significant number of system malfunctions. Approximately one half of the membranes had to be replaced. After the membrane

was replaced, the system's response was tested but additional performance data were not collected. One of the six electrode systems developed a white clogging precipitate. After 22 readings, two others did not function at all. One system probe was accidently set down in the bottom sediment, which resulted in the failure of all its sensors (temperature, dissolved oxygen, pH and conductivity).

Improper membrane installation could account for some of the inconsistencies. Manufacturers' instructions for the replacement of membranes are sometimes vague and confusing. Other possible problems include uncertainty of sensor's depth, electronic drift, and other previously stated factors.

The response times for the in situ dissolved oxygen systems ranged from 20 seconds to 4 minutes; in almost all cases they were greater than the manufacturer's specification. The response time of all sensors of this type (polarographic membrane) will increase with decreasing temperature, and operation at 0°C would thus require longer equilibrium times according to Beckman Instrument communication to NOIC Fact Sheet #76011, 1976.

In this study, the data accuracy (compared to Winkler titration) and precision values were much poorer than the values stated in the manufacturer's specifications.

pH--For field measurements of pH, the 95% confidence interval was ±0.47 pH units. Two systems were very close to the mean of the four systems. Comparable deviations from replicate readings (precision errors) were observed between the shipboard lab and each in situ system. Three responded similarly with changes in station and depth. These systems agreed closely at approximately one half the stations. Another system's values were inconsistent with the sample mean and the pH profile. All systems appeared to function properly and no sensor repair or replacement was necessary. Response time was generally between 1 and 3 mintues. The large uncertainty under field conditions is in agreement with previous studies (8).

Environmental Perturbations

In situ measurements eliminate errors incurred through sampling and sample handling. However, in situ measurements are considered more difficult to make. Standardization and calibration are a serious problem, but when a discrete sample is obtained by water bottle from the ocean "...its temperature and pressure changes. These changes displace rapid equilibria so that by the time our sample has reached the surface its chemical composition has already changed." (4) Contamination from containers, addition or losses of dissolved gasses, settling, precipitation, and decomposition of life forms further contribute to non-in situ measurement error (4). In situ measurements should reflect ambient conditions with greater accuracy than non-in situ techniques. However, in situ measurements also have a set of problems. Instruments which function accurately in the laboratory under closely controlled environmental conditions must still function accurately under a rigorous range of pressure, temperature, water movement, turbidity, light, and chemical and biochemical conditions. Ionic strength and complex formation may shock dissolved oxygen electrodes (F. Millero, University of Miami, pers. comm.).

Temperature compensation methods are somewhat better understood than pressure compensation methods. Plessey and Hydrolab in situ systems include temperature-compensated, bonded strain-gage transducers to measure depth. The YSI 5514 instrument uses a depth-compensated system. However, the combined temperature and pressure effects on dissolved oxygen and pH are only partly understood. Temperature measurements should be pressure-compensated if a high degree of accuracy (±0.01°C) is required, as there is a change in indicated temperature caused by pressure effect on the sensor. An effect as high as 0.81°C at 10,000 meters has been reported (16). Accurate compensation can only be carried out by means of a shipboard computer system; commercial conversion procedures are often inadequate to meet the needs of researchers (A. Bainbridge, GEOSEC, pers. comm.).

The problem of measuring perturbations of measures due to pressure effects, pollutant interference, temperature compensation, and buffering effects is partly due to the lack of standards of reference. The lack of known values of comparison contributes to the problem of defining the meaning of an in situ value. Additional errors may arise due to the unexpected behavior of parameters in situ, and the variability of the quality of standards.

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APPENDIX A

DESCRIPTION OF TWO VARIATIONS OF IN SITU INSTRUMENTATION SYSTEMS

THE PLUNKETT SYSTEM

The Plunkett is a semiautomated system that permits continuous sampling in vertical and horizontal planes. The system was developed in 1969 at the State University of New York, using proven, commercially available components. The Plunkett system has three major components: the sampling unit, the wet lab, and the electronics module. The sampling unit incorporates a submersible centrifugal pump at the lower end of a flexible hose. Vertical sampling can be accomplished from the surface to 80 meters. For horizontal sampling, a second centrifugal pump operates through a hull intake. Parameters measured directly at the pump intake include salinity, temperature, and depth. Seawater is pumped to the wet lab unit on deck where pH, dissolved oxygen, in vivo chlorophyll, and turbidity are routinely measured. Taps are provided for unfiltered seawater for additional analyses.

The electronics module includes signal processing and analytical instruments for determining the height of the sampling unit above the seabed, the depth of the sampling unit below the surface, temperature, pH, dissolved oxygen, salinity from the direct and backup salinometer (thermosalinograph), and underwater photometry. Graphic recording equipment in the form of a multipoint analog stripchart recorder provides a continuous indication of system performance and real-time sensor information, and acts as a backup recording medium in the event of failure of the digital data acquisition system. The data acquisition system can accommodate up to 40 channels.

System Calibration

Calibration of the system was conducted in two separate programs: laboratory and field. The salinometer is calibrated against Standard Seawater.

The thermistor bridge system for direct temperature measurement uses the manufacturer's calibration method and curves. System calibration consists of substituting precision resistors for the thermistor in the bridge. A 12-point calibration is used, and this may be expanded over a narrow temperature range. The resistors are compared to a National Bureau of Standards 1 ohm primary standard resistor. Total accuracy is rated at no greater than the greatest error present, the 0.1°C accuracy of the thermistor. There is no regular calibration of the thermistor against a primary standard; therefore, changes in thermistor characteristics due to physical aging, pressure, damage, etc., would not be apparent to the operator.

The pressure transducer for intake depth measurements is calibrated only

in the field by lowering it on a handline marked in 10-meter increments to 50 meters. The calibration potentiometer is adjusted for a voltage input of 50 mV to the data acquisition system. The transducer is then raised in 10-meter steps, and the voltage on the digital voltmeter is checked. The accuracy of the depth reading is expressed as ±0.5 digit values on the meter.

On-Deck Measurements

The dissolved oxygen probe is calibrated against the Winkler titration using the instrument company's field calibration procedure. This procedure consists of placing the probe in a plexiglass sampling chamber, pumping seawater through the system, and comparing the values obtained with the modified Winkler titration.

pH calibration is conducted by comparison of the probe value against a laboratory pH meter value, submerging the sensor in a standard buffer solution. The probe is equipped with an automatic temperature compensator. The accuracy of the calibration method is reported as ±0.002 at the buffer points and ±0.005 with the buffer and sample in the same range between points.

The in vivo chlorophyll system utilizes a fluorometric determination. Calibration consists of blanking the fluorometer by the Turner and Lorenzen methods, followed by calibration against acetone extractions with a minimum of 15 samples and a standard chlorophyll reference.

The turbidity system is calibrated by blanking the fluorometer with particle-free distilled water. Discrete samples of seawater of known volume are collected from the discharge line. The samples are then filtered through a preweighed millipore filter. The filter is re-weighed, and the weight of particulate matter is plotted as suspended solids per volume of seawater sample by which fluorometer values can be checked (17).

THE "FISH"

The "fish," which was developed and used by the Institute of Marine Resources of the University of California, Berkeley, is towable at speeds up to 5 knots, and can be programmed for sampling from the surface to 30 meters, permitting both vertical and horizontal profiling. The system monitors the following parameters to the indicated accuracies:

- Depth: 0-30 m ±0.1 m
- Temperature, full range: ±0.02°C
- Conductivity, full range: 0.3%
- Dissolved oxygen, full range: 1% of full range
- pH, sulphide ion, and Eh: within 1 mV of electrode voltage
- Ambient light: detects changes within 1% of full scale

Similar design concepts have been available from commercial manufacturers such as the Hydrospace Corp., Towed Automatic Profiler, and Hermes Ltd., which offers the "Batfish."

Calibration Techniques for the "Fish"

This type system has unusual calibration requirements. The parameter values are recorded with a precision of ±1 digit on either a 16-mm single frame movie camera or alternately on a digital cassette recorder. In turn, the basic accuracy of the overall system is dependent upon the accuracy of the internal reference voltage. Therefore, the aim of the calibration procedure was to ensure the internal reference accuracy rather than traceability to a defined standard. For example, traceability of the temperature sensor to the manufacturer's test and calibration of the thermistor.

Dissolved oxygen calibration is performed in a seawater bath containing a sample of fully oxygenated water of known salinity. The sample is agitated to read oxygen saturation equilibrium. Calibration of the dissolved oxygen probe is performed every time the membrane is replaced.

pH calibration is accomplished with standard buffer solutions and is corrected for alkaline error due to the presence of cations and temperature effects.

The sulfide sensor is calibrated in the laboratory with a solution of variable S activity. The solution is made by bubbling gaseous H_2S in a 0.25 molar Na_2S and 0.5 molar KCL solution and by changing the pH by adding 1 molar acetic acid.

The Eh sensor is checked occasionally by measuring the Eh potential of a standard oxidizing solution that has an Eh value of 430 mV. Experience indicates that the Eh value obtained is within 10 mV of the standard value without any special electrode cleaning.

The conductivity sensor is calibrated against a temperature-compensated laboratory-grade salinometer. Pressure effects are neglected during calibration but corrections for pressure are incorporated during the data analysis phase using the Bradshaw and Schleicher tables (18).

APPENDIX B

EXPERIMENTAL CRUISE FOR COMPARISON OF CALIBRATION ACCURACIES

An intercomparison cruise was conducted on April 13, 1977, in Monterey Bay aboard the Ship R/V Oconostota for the purpose of directly comparing the in situ measurement accuracy of instruments measuring dissolved oxygen, conductivity (salinity), temperature and pH to laboratory results. Four in situ systems, each with an individual operator, were simultaneously operated at a number of discrete depths to a maximum of 50 meters at five widely spaced stations to offer a range of environmental variability. The station locations sampled appear in Figure 1. All analytical systems were calibrated before the cruise according to the manufacturers' recommended procedures: dissolved oxygen using air-saturated water; conductivity using Standard Seawater; and pH using buffer solutions. Temperature and pressure sensors were calibrated by the manufacturer using constant temperature baths and high pressure chambers respectively. LFE Environmental Labs supported Interstate's staff by calibrating instruments, performing laboratory analyses, and by participating in the supervision of cruise operations.

Laboratory analysis for the traceability of standards for dissolved oxygen and conductivity were performed at LFE's certified laboratory located in Richmond, California. To ensure proper handling of samples from point of origin to laboratory, senior laboratory personnel participated in the operation, collected the samples, and were responsible for transport.

In Situ Instruments

Specifications for parameters measured by each of the in situ systems and laboratory systems (shipboard and shore based) used appear at the end of this section in Tables B-1 to B-11. In situ salinity was measured with in situ and laboratory systems using either inductive coupling or multiple electrode techniques. Dissolved oxygen membrane polarographic electrodes and glass pH electrodes were used in both laboratory and in situ measurements. Temperature-compensated bonded strain gage transducers were used by the Plessey and Hydrolab system to measure in situ depth. Temperature sensors were all resistance transducers with one platinum transducer and four types of thermistors.

Most of the systems were capable of measuring the full pH range, 0 to 14. All systems were capable of measuring temperature from 0 to 35°C, and three systems could accurately measure in the 5 to 45°C range. All instruments were capable of measuring dissolved oxygen concentration levels from 0 to 20 ppm. Many scales were available for the measurement of electrolytic conductivity in mS/cm. The most common range of measurement was 0 to 60 mS/cm. The systems predominantly employed an automatic temperature compensation arrangement.

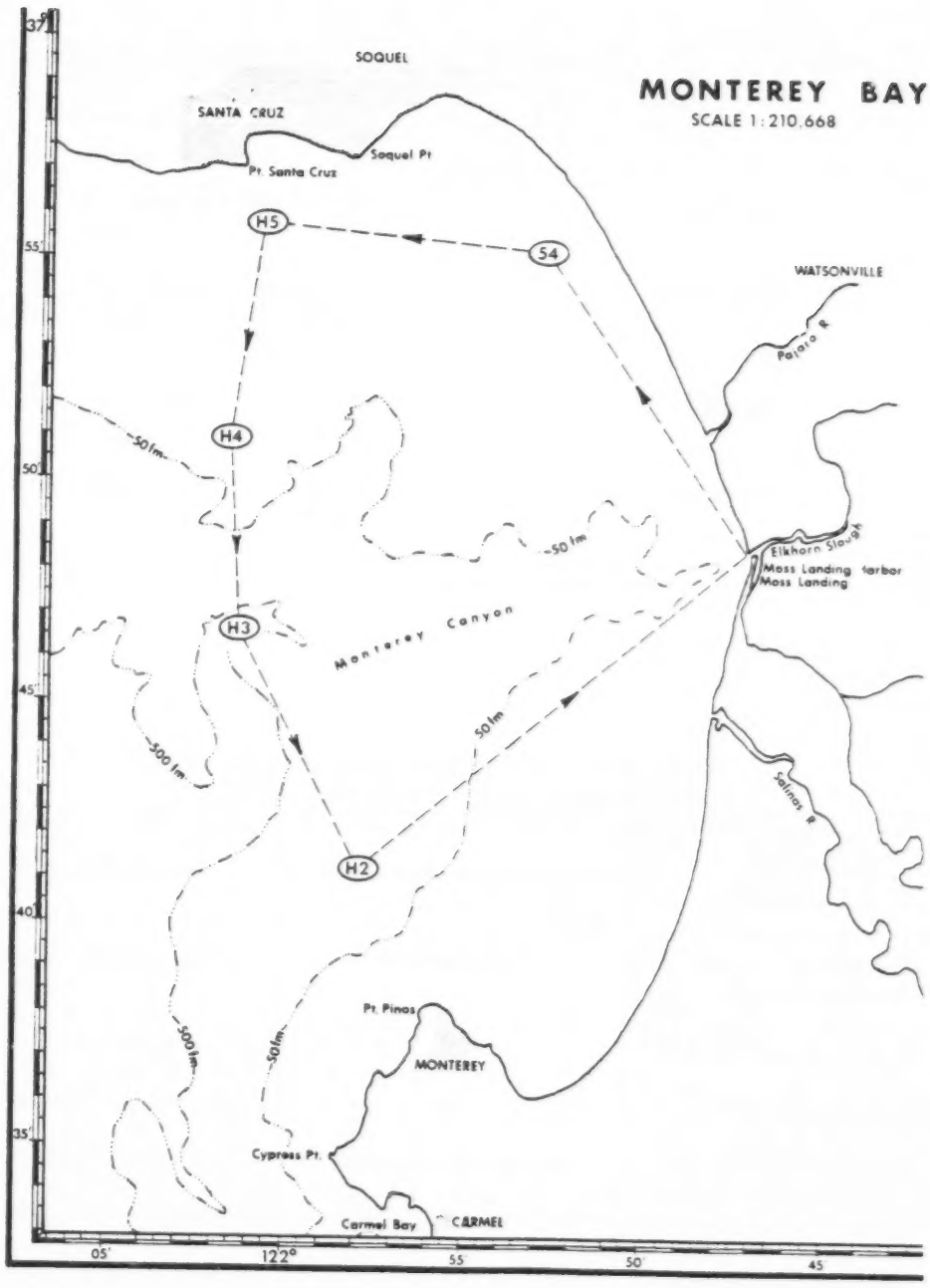

Figure 1. Intercalibration cruise sampling station locations.

TABLE B-1. IN SITU SYSTEMS USED FOR EXPERIMENTAL CRUISE

Manufacturer	Parameters Measured
Horiba:	Dissolved Oxygen, pH, Conductivity, Temperature.
Hydrolab:	Dissolved Oxygen, pH, Conductivity, Temperature, Depth (Pressure).
Martek:	Dissolved Oxygen, Temperature, Conductivity, pH.
Plessey:	Conductivity, Temperature, Depth (Pressure).

TABLE B-2. LABORATORY METHODS USED ON DISCRETE SAMPLES FOR EXPERIMENTAL CRUISE

Method or Instrument	Parameters Measured	Where Measured
Reversing Thermometer	Temperature	Shipboard Laboratory
Orion pH meter	pH	Shipboard Laboratory
Beckman pH meter	pH	Shipboard Laboratory
YSI D.O. meter	Dissolved Oxygen	Shipboard Laboratory
Winkler titration	Dissolved Oxygen	Shore Based Laboratory
Beckman Salinometer	Salinity	Shore Based Laboratory

TABLE B-3. SUMMARY OF SYSTEM ACCURACIES

MANUFACTURER	SYSTEM MODEL	ESTIMATED COST	CONDUC-TIVITY	SALINITY	TEMP-ERATURE	pH	DISSOLVED OXYGEN	DEPTH
Horiba	U-7	2,950	±2.5 mS/cm	N.A.	±0.5°C	±0.1	±1.0 mgO_2/l	N.A.
Hydrolab	Surveyor-6D12	5,000	±0.5% fs	0.5 ppt	±0.25°C	±0.1	±0.5% fs	±1.5% fs
Martek	MK V	4,950	±0.5 mS/cm	±0.5 ppt	±0.1°C	±0.1	±0.1 mgO_2/l	±0.1% fs
Plessey Environmental Systems	CTD9400-5	20,000	±0.03	N.A.	±0.02°C	±0.02	±2% fs	± .25% fs

Information from manufacturer's product bulletins

fs = full scale
N.A. = not available

TABLE B-4. HORIBA: U-7 WATER QUALITY CHECKER

Parameter	Method of Measurement	Range of Measurement	Temperature Compensation
pH	Glass electrode	0 to 14 pH units	Automatic 0 to 40°C
Temperature	Thermistor	0 to 40°C	Not Required
Dissolved Oxygen	Membrane type Galvanic cell	0 to 20 mgO_2/l	Automatic 0 to 40°C
Conductivity	4-electrode sensor	0-50.0 mS/cm or 0-100.0 mS/cm or 0-1000 mS/cm	Not Available

Indicator: Light-emitting diodes - 3 digits.

Power Required: Rechargeable battery (nickel-cadmium cell) or 117 Vac.

Cable Length: 2. meters with an optional length of 10 meters.

Weight: Instrument - 0.63 kg
Sensor - 0.82 kg
Shipping weight - 6.35 kg with case

TABLE B-5. HYDROLAB: 6D SURVEYOR

Parameter	Method of Measurement	Range of Measurement	Temperature Compensation
Temperature	Thermistor	-5 to 45°C	Not Required
Conductivity	4-electrode a-c cell; pure nickel electrodes	0 to 1000 µS/cm 0 to 10,000 µS/cm 0 to 100,000 µS/cm	Automatically corrected to 25°C for salinities up to 35 ppt and temperatures between 0 and 45°C
pH	pH electrode, reference electrode, pair	2 to 12 pH units	standard correction 0 to 45°C
Depth	Pressure transducer	0 to 200 meters	Automatic
Dissolved Oxygen	Passive polarographic cell	0 to 10 mgO_2/l 0 to 20 mgO_2/l	Automatic 0 to 45°C

Power Requirement: (Circulatory) 12 vdc.

Cable Length: 100 meters

Size: Length 53 cm, Diameter 17 cm

Weight: 7 kg

TABLE B-6. MARTEK: MARK V DIGITAL WATER QUALITY ANALYZER

Parameter	Method of Measurement	Range of Measurement	Temperature Compensation
Temperature	Thermolinear array	-5 to 45°C	Not Required
pH	Combination pH electrode with silver-silver chloride reference	0 to 12 pH units	Automatic
Conductivity	Platinized nickel electrodes	0 to 1000 µS/cm or 0 to 100 mS/cm	Not Required
Dissolved Oxygen	Polarographic gold-silver electrode	0 to 20 mgO_2/l	Automatic with in situ stirrer

Power Required: Regulated self-contained internal rechargeable battery pack with built in charging circuit, external 18-36 Vdc, or 105-125 Vac, (210-250 Vac), 50/60 Hz.

Cable Length: 50 meters

Size: 5.72 cm x 38.1 cm

Weight: 0.9 kg

TABLE B-7. PLESSEY ENVIRONMENTAL SYSTEMS: MODEL 9400 TELEMETERING SENSOR SYSTEM

Parameter	Method of Measurement	Range of Measurement	Temperature Compensation
Temperature	Platinum Resistance Transducer	-2 to 35°C	Not Required
Conductivity	Inductive Coupling Technique	0 to 60 mS/cm	Automatic temperature and pressure correction
Depth	Bonded Strain-gage	0 to 300 meters 0 to 600 meters optional	Automatic

Power Required: 150-250 mA constant current at a minimum of 33 V dc plus cable drop; equipped with strip chart recorder.

Cable Length: 300 meters (moored)
600 meters (profiling)

Weight: 13.6 kg (in air)
9.1 kg (in water)

TABLE B-8. YELLOW SPRINGS INSTRUMENTS: MODEL 57 DISSOLVED OXYGEN METER

Parameter	Method of Measurement	Range of Measurement	Temperature Compensation
Temperature	Thermistor	-5 to 45°C	Not Required
Dissolved Oxygen	Polarographic electrode	0-5 mgO_2/l 0-10 mgO_2/l 0-20 mgO_2/l	Automatic from -5 to 45°C

Power Required: Two disposable "C" size carbon zinc batteries (provide approximately 1000 hours operation).

Size: 21 x 27.5 x 9 cm

Weight: 2.5 kg

Cable Length: 15 meters

TABLE B-9. BECKMAN SELECT-MATE

Parameter	Method of Measurement	Range of Measurement	Temperature Compensation
pH	Combination electrode	0 - 14 pH units	Manual
Power Required: 9 Volt battery operated (120/220V - 50/60 Hz optional). Capability: Lab System Only Size: 26 x 22 x 12 cm Weight: .68 kg (1.5 lbs)			

TABLE B-10. ORION pH METER

Parameter	Method of Measurement	Range of Measurement	Temperature Compensation
pH	Combination electrode	0 - 14 pH units	Manual
Power Required: 120 Vac, 50/60 Hz Capability: Lab System Only Size: 17 x 20 x 20 cm Weight: 2.3 kg (5.1 lbs)			

TABLE B-11. BECKMAN RS 7-C INDUCTION SALINOMETER

Parameter	Method of Measurement	Range of Measurement	Operating Temperature
Salinity	The ratio of conductivities and salinity is read directly from tables, such as the UNESCO International Oceanographic tables.	0 to 49 parts per thousand salinity	0 to 40°C Accuracy ±1°C
Power Requirement: 120 Vac, 50/60 Hz Capability: Moist sea atmosphere requirements of MIL-E-16400, and shipboard vibration MIL-STD-167 Type 1. Size: 51 x 41 x 28 cm Weight: 13.6 kg (30 lbs)			

GLOSSARY

The scope of this glossary is limited to the special area of knowledge and word usage applicable to the text of this report. The definitions and terms were researched from the sources of information listed at the end of the Appendix. Most definitions have been quoted verbatim from these references.

accuracy: 1. The extent to which the results of a calculation or the readings of an instrument approach the true values of the calculated or measured quantities, and are free from error. 2. Conforming exactly to truth or to a standard. 3. When applied to methods of analysis, a measure of the error of a method may be expressed as a comparison of the amount of element or compound determined or recovered by the test method and the amount actually present.

analog: Pertaining to data in the form of continuously variable physical quantities.

automatic data processing (ADP): The utilization of electronic data processing equipment (computer) to perform any variety of tasks involving informational data.

baseline: A main line taken as or representing a base. The point or line from which a start is made in an action or undertaking.

baseline assessment survey: The planned sampling or measurement of parameters at set stations or in set areas in and near disposal sites for a period of time sufficient to provide synoptic data for determining water quality, benthic, or biological conditions as a result of ocean disposal operations.

benthic: That portion of the marine environment inhabited by marine organisms which live permanently in or on the bottom.

buffer: A solution selected or prepared to minimize changes in hydrogen ion concentration which would otherwise occur as a result of a chemical reaction.

calibrated accuracy: When applied to methods of analysis, the difference between the indicated parameter value and its accepted value (known value); determined by calibrating an uncontaminated sensor in the measuring system.

calibration: 1. To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device, or

the correct value for each setting of a control knob. 2. To determine the settings of the control devices so that a system will operate or perform within certain limits. 3. Periodic standardizations of equipment and instruments.

cation: A positively charged atom or group of atoms, or a radical, which moves to the negative pole (cathode) during electrolysis.

coastal waters: Ocean waters seaward to the territorial limits and waters along the coastline (including inland streams) that are influenced by the rise and fall of the tide.

conductivity: Measure of the ability of a solution to carry electrical current and thus, a measure of ion concentration in water. High ion concentrations may render water unpalatable or even toxic to plants and animals.

continuous profiler: As applied to water quality measuring systems, implies a system that makes uninterrupted measurements of parameters as a function of the sensor package depth.

criteria: A standard on which a judgment or decision may be based. (See standard.)

data: Any representations, such as characters or analog quantities, to which meaning might be assigned.

data acquisition: The phase of data handling that begins with the sensing of variables and ends with a magnetic recording or other record of raw data; may include a complete radio telemetering link.

data base: A collection of information in machine-readable form.

data processing (information processing): Any operation or combination of operations on data, including everything that happens to data from the time they are observed or collected to the time they are destroyed.

digital: Relating to calculation by numerical methods or by discrete units.

dissolved oxygen (DO): The oxygen in sewage, water, or other liquid usually expressed in parts per million (ppm). Oxygen has a low solubility in and is nonreactive with water. Its solubility is dependent on water temperature and partial pressure in accordance with Henry's Gas Law. Because of this temperature dependence, DO tends to be critical during periods of high temperatures since oxygen solubility is at a minimum while biological activity, and its corresponding oxygen demand, is at a peak. Dissolved oxygen is one of the key parameters in assessing the quality or degree of pollution in water. Its measurement is required for waste water treatment, fisheries research, baseline studies, and enforcement monitoring.

Eh: The redox potential measured in millivolts. Positive values indicate the presence of surplus oxygen. Negative voltage indicates a reducing environment, most commonly caused by the presence of sulfides. (See redox potential.)

electrode: The conductor by which current enters and leaves an electrolyte when subjected to an externally impressed potential.

electrolyte: Any substance which, in solution or fused, exists as electrically charged ions that make the liquid capable of conducting a current. Seawater is an electrolyte.

electronic data processing (EDP): Processing data by equipment that is predominantly electronic in nature, such as an electronic digital computer.

error: 1. Any discrepancy between a computed, observed, or measured quantity and the true, specified, or theoretically correct value of that quantity. 2. Error of measurement may be systematic or accidental. Accidental errors are slight variations that occur in successive measurements by the same observer. Causes are generally intangible. They may follow the law of chance.

GEOSECS: The acronym for Geochemical Ocean Sections, one of the major programs of the International Decade of Ocean Exploration, a multinational cooperative study of the world oceans during the period 1970-1980.

hysteresis: An effect, involving energy loss, found to varying degrees in magnetic, electric, and elastic media when they are subjected to variation by a cyclical applied force.

in situ: 1. In the original location (in the environment). 2. In the natural or original position.

in situ system: Typically, seawater sampling equipment and various analytical instruments which measure various parameters while on station. The data from the instruments are displayed in real time on strip chart analog recorders, and the same data are digitized on magnetic tape for subsequent computer analysis. (See pump-thru-system.)

in vitro: Pertaining to a biological reaction taking place in an artifical apparatus (in glass or in a test tube, beaker, etc.).

in vivo: Pertaining to a biological reaction taking place in a living cell or organism.

ion: Electrically charged atom or group of atoms.

linearity: The maximum deviation between an actual instrument reading and the reading predicted by drawing a straight line between the upper and lower calibration points.

mariculture: The cultivation of marine organisms by exploiting their natural environment.

marine: Pertaining to the sea.

measurement: The process of determining the value of some quantity in terms of a standard unit.

meter sensitivity: The accuracy with which a meter can measure a voltage, current, resistance, or other quantity.

metrology: The science of measurement.

monitoring: 1. The act of observing and recording laboratory and field environment test conditions, test specimen responses, and performance parameters. 2. The acquisition of data at approximately the same location and at some fixed frequency. (See measurement.)

monitoring station: Particular point at which representative samples of a body of water are collected periodically.

multiparameter capability: Ability to measure several constituents simultaneously.

nutrients: Substances essential to bacterial growth and function. Chief among these are carbon, nitrogen, phosphorus, and sulfur, but a number of trace elements have been shown to be essential to growth (K, Ca, Mg, Fe, Mn, Zn, Co, Cu, and Mo).

ocean instruments: Devices which measure parameters of the marine environment, including oceans, estuaries, large fresh water bodies, the air directly above these waters, and the sea floor below.

ocean: Those waters of the open seas lying seaward of the baseline from which the territorial sea is measured, as provided for in the Convention on the Territorial Sea and the Contiguous Zone.

ocean water: Water having between 20,000 and 40,000 mg/l dissolved material whose ionic ratios correspond closely to those specified in "Standard Specification for Substitute Ocean Water," ASTM Method D1141-52 (1971).

operational: Ready for or in condition to undertake a destined function.

oxidation reduction potential (ORP): See redox.

parameter: A measurable biological, chemical, or physical characteristic, e.g., temperature, pressure, currents, etc., the size of sediment grains or fish.

parts per million (ppm): A ratio of pounds per million pounds, grams per million grams, etc. Approximately equal to milligrams per liter, expressing the concentration of a specified component.

pH (Hydrogen Ion Concentration): A term used to describe the hydrogen-ion activity of a system. The pH of a solution is defined as the negative logarithm of hydrogen ion concentration, and is thus an expression of the acid or alkaline character of the solution. A solution of pH 0 to 7 is acid, pH of 7 is neutral, pH over 7 to 14 is alkaline. pH is of major importance in dealing with treatment of water and wastewater since it affects taste, corrosivity, chemical reactions and biological activity. Since certain wastes tend to be strongly acidic or basic, sharp changes

or extremes of pH may indicate the presence of pollution in receiving waters.

physical parameter: Most common, nonchemical characteristics of water, including color, specific conductance, threshold odors, turbidity, and dissolved and suspended solids.

pollution: The addition of sewage, industrial waste, or other harmful or objectionable material to water at a concentration or in sufficient quantity to result in measurable degradation of water quality.

precision: 1. The quality of being exactly or sharply defined or stated. 2. The degree of refinement with which an operation is performed or a measurement stated. 3. Adapted for extremely accurate measurements. 4. Held to low tolerance in manufacture. 5. When applied to methods of analysis, a measure of the reproducibility of a method when repeated on a homogeneous sample under controlled conditions, regardless of whether or not the observed values are widely displaced from the true values as a result of systematic or constant errors present throughout the measurements. Precision can be expressed by the standard deviation. 6. Narrowness of limits within which one may assume true value of measured quantity--the narrower the limits, the better the precision.

prototype: A model suitable for use in complete evaluation of form, design, and performance.

pump-thru-system: Typically water is pumped from known depths to the ship's deck, where it is conducted to instruments which measure salinity, temperature, dissolved oxygen, pH. In situ sensors measure pump depth, temperature, and submarine light transmission. (See vertical profile.)

quality assurance: Testing and inspecting all of or a portion of the final product to ensure that the desired quality level of product reaches the customer.

quasi: Having some resemblance.

random error: An error that can be predicted only on a statistical basis. (See error.)

range: 1. The difference between the maximum and minimum of a variable quantity. 2. When applied to methods of analysis, the difference between the smallest and largest of n observations is also closely related to the standard deviation.

reagent: A substance, chemical or solution used in the laboratory to detect, measure, or otherwise examine other substances, chemicals, or solutions.

redox potential: Voltage difference at an inert electrode immersed in a reversible oxidation-reduction system; measurement of the state of oxidation of the system. Also known as oxidation-reduction potential (ORP). (See Eh.)

reliability: 1. The probability that a component part, equipment, or system will satisfactorily perform its intended function under given circumstances, such as environmental conditions, limitations as to operating time, and frequency and thoroughness of maintenance for a specified period of time. 2. The amount of credence placed in a result. 3. The precision of a measurement, as measured by the variance of repeated measurements of the same object.

repeatability: The degree to which an instrument or technique provides the same result when exposed to identical input conditions.

replicate: One of several identical experiments, procedures, or samples.

rosette type sampler: A water sampling device consisting of a group of six or more cylinders arranged in a circular or rose pattern frequently equipped with a sensor package for making simultaneous measurements. Used to obtain multiple samples on a single cast.

representative sample: Water sample whose measured values are characteristic of the body of water from which the sample has been taken.

reversing thermometer: A mercury-in-glass thermometer which records temperature upon being inverted and thereafter retains its reading until returned to the first position.

salinity: Total amount of dissolved salts ($^{\circ}/_{\circ\circ}$) in seawater; commonly the dominant factor controlling density of seawater. The measurement of salinity (and temperature) can be used in the open ocean as tags to identify water masses as they spread laterally between other masses, or move along the ocean floor.

sampling: Obtaining small representative quantities of materials for analysis.

seawater: The water of the seas, distinguished from fresh water by its appreciable salinity. The distinction between the usage of salt water and seawater is not very sharply drawn. Commonly, seawater is used as the antithesis of specific types of fresh water, as river water, lake water, rainwater, etc., whereas salt water is merely the antithesis of fresh water in general.

sensitivity: The ability of the output of a device, system, or organism to respond to an input stimulus. Mathematically, the ratio of the response or change induced in the output to a stimulus or change in the input. The degree to which a substance can be detected in the presence of interfering components which have properties differing only very slightly from those of the substance.

sensor (primary detector; sensing element): The generic name for a device that senses either the absolute value or a change in a physical quantity such as temperature, pressure, flow rate, or pH, or the intensity of light, sound or radio waves and converts that change into a useful input signal for an information-gathering system; a television camera is therefore a sensor, and a transducer is a special type of sensor.

stability: The measure of the length of time a measuring system, once calibrated, continues to measure the actual parameter value within the calibrated accuracy without the need for readjustment or recalibration. Stability performance is based upon the measurement of standard calibrating solutions with an uncontaminated sensor.

standard: 1. An accepted reference sample used for establishing a unit for the measurement of a physical quantity. 2. Constituting or affording a standard for comparison or judgment.

Standard Seawater (normal water): Water whose chlorinity lies between 19.30 and 19.50 parts per thousand, determined to within ±0.001 per thousand, which is used to calibrate or standardize salinity measuring devices or methods.

standardization: 1. The adoption of generally accepted uniform procedures, dimensions, materials, or parts that directly affect the design of a product or a facility. 2. The process of establishing by common agreement engineering criteria, terms, principles, practices, materials, items, processes, and equipment parts and components.

standardized product: A product that conforms to specifications resulting from the same technical requirements.

STD (salinity-temperature, depth recorder): An instrument for continuously measuring the temperature, electrical conductivity, and depth. It automatically determines water salinity from the temperature-conductivity-salinity relationships.

synoptic: In general, pertaining to or affording an overall view.

system reliability: The probability that a system will accurately perform its specified task under stated environmental conditions. (See reliability.)

thermistor: A resistive circuit component, having a high negative temperature coefficient of resistance, so that its resistance decreases as the temperature increases; a stable, compact, and rugged two-terminal ceramic-like semiconductor bead, rod, or disk.

titration: A method of analyzing the composition of a solution by adding known amounts of a standardized solution until a given reaction (color change, precipitation, or conductivity change) is produced.

transient response: Rate at which a system responds to a step change.

transmissometer: A light-path device for measuring attenuation of light in water due to scattering and absorption.

turbidimeter: An instrument for measurement of turbidity, in which a standard suspension usually is used for reference.

turbidity: 1. The property in water that inhibits light penetration. Turbidity is caused by suspended and colloidal matter, either from natural

erosion or industrial and domestic waste. 2. Highly turbid water may contain large amounts of organic material acting as food for microbes, producing further growth and, consequently, increasing turbidity.

validation: The act of testing for compliance with a standard.

vertical profile: A graphical representation whose ordinate shows the variation of some oceanographic quantity along a straight line against horizontal distance on this line as abscissa.